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DEVELOPMENT OF MODERN METHODS FOR DETERMINATION OF
STABILIZERS IN PROPELLANTS.

by

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ABSTRACT

This document is the final report required by a task from the Directorate of Ammunition Engineering Service (DAES) aimed at developing modern methods of monitoring the chemical stability and remaining safelife of gunpowders stocked by the Canadian Forces. This report begins with a review of the chemistry of propellant ageing and the various techniques available to monitor chemical stability. This is followed by a description of the development of two fast, reliable and efficient high-performance liquid chromatography methods. Finally, the application of these two methods for the surveillance programme of diphenylamine or ethylcentralite-stabilized gun propellants are discussed.

RÉSUMÉ

Ce document est le rapport final d'une tâche du Directeurat-Service technique des munitions (DSTM) dont le but était le développement de méthodes modernes pour la surveillance de la stabilité chimique et de la durée de vie résiduelle des poudres à canon entreposées par les Forces canadiennes. Dans un premier temps, on brosse un tableau de la chimie du vieillissement des poudres à canon ainsi que les diverses techniques utilisées pour vérifier leur stabilité chimique. Par la suite, on donne une description détaillée du développement de deux méthodes d'analyse rapides, reproductibles et efficaces basées sur la chromatographie liquide à haute performance. Enfin, on étudie l'application de ces deux méthodes pour un programme de surveillance des poudres à canon stabilisées à la diphenylamine ou à l'éthylcentralite.

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EXECUTIVE SUMMARY

Propellants stored in bulk (prior to filling) or in ammunition are among the biggest items in the DND inventory. These propellant formulations contain nitrate esters, such as nitrocellulose (NC) and nitroglycerine (NG), which tend to decompose with time, releasing nitrogen oxides. If not removed, these nitrogen oxides react catalytically to accelerate the nitrate ester's degradation and, as a result, heat is produced. Therefore, self-ignition may occur and several disasters that have occurred throughout the world bear testimony to this. To remedy this situation, stabilizers such as diphenylamine and ethylcentralite are added to gun propellant formulations. These stabilizers react easily with nitrogen oxides and prevent self-ignition from occurring. However, with time there is a depletion of the effective stabilizer level in the gunpowder. Therefore, an effective surveillance programme, that periodically monitors the stabilizer content of propellants, is essential for the maintenance of safety and the maximum use of resources.

The current Canadian gun propellant surveillance programme is based on the Abel heat test and the colour test. These tests are outdated, empirical, and above all, under specific conditions, can lead to misleading results. Such a situation is potentially dangerous and for this reason alone, these obsolete tests must be replaced by modern tests. Furthermore, the present propellant surveillance equipment in Canadian depots is old and in need of replacement. Therefore, this would be the most opportune time to replace the Abel heat test and the colour test with a modern, efficient and reliable test. As a result, the Canadian Forces (CF) assigned to the Defence Research Establishment Valcartier (DREV) a task aimed at replacing the obsolete Abel heat test and the colour test with a modern analytical chemistry method; the present document is the final report on this task.

In this document, there is a review of the chemistry of propellant ageing and the various techniques available to monitor the chemical stability. Afterwards, the rationale behind the choice of high-performance liquid chromatography (HPLC) is discussed. This is followed by the description of the development of two fast, reliable and efficient HPLC methods. Finally, the application of these two methods for the surveillance programme of diphenylamine or ethylcentralite-stabilized gun propellants, as well as the establishment of sentencing criteria, are discussed.

In the future, these two methods will be used for the acceptance and the surveillance of the chemical stability of the propellants purchased, used and stocked by the Canadian Forces. As a result, the CF will have a new surveillance programme that is more efficient, reliable and safe. Moreover, the CF will now be able to collect data and construct meaningful databases. In this manner, it will be possible to develop an expertise and a history of propellant ageing and therefore make sound predictions on the service life of munitions. In conclusion, this modern surveillance programme will promote an enhanced safety and maximize the use of resources, an important consideration given the fact that propellants are the biggest items in the DND inventory and in the light of the recent budget cuts experienced by DND.

ABBREVIATIONS

A_i	Area of the compound i peak in the chromatogram
A_{IS}	Area of the internal standard peak in the chromatogram
ACN	Acetonitrile
CF	Canadian Forces
DAP	Diamylphthalate
DBP	Dibutylphthalate
DEP	Diethylphthalate
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DND	Departement of National Defence
DNT	Dinitrotoluene
DPP	Diphenylphthalate
DPA	Diphenylamine
EC	Ethyl Centralite
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HPLC	High-Performance Liquid Chromatography
IR	Infra Red
k	Retention factor
K_{Fi}	Response factor for Compound i
m_i	Mass of Coumpound i in the standard solution
m_{IS}	Mass of the internal standard in the solution
M_p	Mass of the powderdissolved in the sample solution
MeOH	Methanol
MWCC	Molecular Weight Corrected Concentration
N	Column plate number

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NATO	North Atlantic Treaty Organization
NBS	n-Butylstearate
NC	Nitrocellulose
NG	Nitroglycerine
NMR	Nuclear magnetic resonance
NQ	Nitroguanidine
RES	Residual effective stabilizer
R_s	Resolution
STANAG	Standardization Agreement
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
t_0	Retention time for an unretained solute
t_r	Retention time for a retained solute
UV	Ultraviolet
W_r	Bandwidth at half height
α	Ratio of k values for two adjacent peak

1.0 INTRODUCTION

Gun propellant formulations contain ingredients such as nitrocellulose (NC) and nitroglycerine (NG). These nitrate esters tend to decompose with time, releasing nitrogen oxides. If not removed, these nitrogen oxides act catalytically to accelerate the nitrate ester's degradation. As a result, spontaneous ignition may occur and the several disasters that have occurred since the introduction of NC-based gun propellants in the last century bear testimony to this.

For instance, in 1905, on the Japanese battleship "Mikasa", some English nitroglycerine powder exploded with the loss of 600 lives (1, 2). An explosion of the ammunition magazine of the French battleship "Jena" in 1907 resulted in the loss of 110 lives (1, 2) and a similar catastrophe occurred on the battleship "Liberté" in 1911 (1, 3). After World War I the storage of unstable powders caused several catastrophes e.g. in Poland there were explosions of the magazines in the Warsaw Citadel in 1924 and at Witkowitz in 1927, and in France at Bergerac in 1928 (3). Recent fires in Finland (4), in Australia (5) and in Sweden (6) were also caused by the spontaneous ignition of gun propellants. To prevent such disasters from occurring, stabilizers such as diphenylamine (DPA) or ethyl centralite (EC) are added to gun propellant formulations.

These stabilizers react easily with nitrogen oxides and prevent auto-ignition from occurring. The reactions of these compounds are complex and many daughter products are formed. Some of these products act as stabilizers, but others do not and there is a depletion of the effective stabilizer level in the gunpowder with time. Therefore, the stabilizer content of propellants must be monitored periodically to assess their remaining "safe life" and to dispose of those lots that are likely to undergo auto-ignition.

The current Canadian gun propellant surveillance programme is based on the Abel heat test and the colour test. These tests are outdated and above all, under specific conditions, can lead to misleading results. Such a situation is potentially dangerous and for such reasons alone, the obsolete Abel and colour tests must be replaced by a modern test.

In fact, recent investigations with modern analytical instrumentation have given a more accurate description of propellant degradation and therefore, tests that were used twenty years ago have been replaced, in several countries, by more modern methods whose superiority over the older tests is generally accepted. Furthermore, the present equipment in Canadian depots is old and in need of replacement. Therefore, this would be the most opportune time to replace the Abel heat test and the colour test with a modern, efficient and reliable test.

As a result, the Canadian Forces (CF) assigned DREV Task DAME 096 entitled "Development of modern methods for determination of stabilizers in propellants". This task was aimed at replacing the obsolete Abel heat test and the colour test with a modern analytical chemistry method based on High-Performance Liquid Chromatography (HPLC). The present document is the final report on DAME Task 096.

The work reported here was done at DREV during the period between April 1991 and December 1993 under Task 031XM-11.

2.0 THE CHEMISTRY OF PROPELLANT AGEING

2.1 Introduction

Nitric esters are sensitive to thermal stress. The CO-NO₂ bond is split homolytically (7):



The cause of this is the low binding energy of the CO-NO₂ bond, approximately 160 KJ/mole (8, 9) compared to 414 KJ/mole for a typical C-H bond. Consequently, the nitrate esters decompose even under normal storage temperatures.

This homolytical splitting of the CO-NO₂ bond produces the reactive NO₂ radical, a strong oxidizing agent, and the alkoxy radical. These initial products are highly reactive. Consequently, this initial phase is rapidly followed by a series of secondary reactions. These reactions are exothermic since radical species are involved. As a result, heat is produced and the propellant temperature rises since propellants, being plastic materials, are not good heat conductors. This temperature rise increases the rate of the homolytic splitting of the nitric esters and the subsequent secondary reactions will in turn further increase the temperature. If nothing is done to stop this autocatalytic action the propellant temperature will increase until the occurrence of auto-ignition and, as mentioned in the introduction, several accidents in the past bear testimony to this autocatalytic effect. To prevent the autocatalysis effect from occurring, stabilizers such as diphenylamine or ethyl centralite are added to gun propellant formulations.

Between the end of the last century and the middle of this one, several studies were done to elucidate the mechanisms by which these molecules stabilize the

propellant. Some of these studies are referenced in the classic work of Schroder et al. (10, 11). These studies, and modern ones, have clearly demonstrated that stabilizers act as scavengers of nitrogen oxides and in doing so they remove nitrogen oxides from the system before they can catalyze the thermolysis reaction.

As a result, during storage the stabilizer continues to react more and more with the nitrogen oxides and gives rise to several reaction products. The purpose of studying the chemistry of ageing is to find out which reaction products are formed, to what extent and what is their order of appearance. These issues will be discussed in this section. However, before going into more detail in the chemistry of ageing, we should first discuss, for the sake of clarity, some rules of nomenclature for DPA and EC derivatives.

2.2 Nomenclature

The chemical structure diagrams for DPA and EC are illustrated in Fig. 1. In order to distinguish the various positions on the two phenyl groups a numbering system is also included in Fig. 1.

The reaction of nitrogen oxides with DPA and EC involves nitrosation and nitration. Nitrosation is the addition of a nitroso group ($-NO$) to the DPA or EC molecule; this nitroso group can be attached to the nitrogen (N-nitroso) or to a carbon atom in the phenyl groups (C-nitroso). Nitration is the addition of a nitro group (NO_2) and, similarly, the nitro group can be attached to the nitrogen atom (N-nitro) or to a carbon atom of the phenyl groups (C-nitro). For C-nitroso and C-nitro, the position on the phenyl group must be specified in order to distinguish the isomers, for example 2- NO_2 -DPA (Fig. 2A) versus 4- NO_2 -DPA (Fig. 2B). For higher levels of substitution the two phenyl groups are differentiated by adding a prime (') for the positions of the

phenyl group, for example 2,4-di-NO₂-DPA (Fig. 2C) versus 2,4'-di-NO₂-DPA (Fig. 2D). The same principles apply for nitroso substitution, for example N-NO-DPA (Fig. 2E) and 4-NO-DPA (Fig. 2F). Figure 2G illustrates a blend of nitroso and nitro as in N-NO-2,4'-di-NO₂-DPA.

Figure 3 illustrates the same rules applied to EC. However, in this case there are two types of daughter products. First, there are the C-nitro derivatives of EC, as shown in Figs. 3A and 3B for 4-NO₂-EC and 4-4'-di-NO₂-EC. Secondly, monoaromatic derivatives are formed by the cleavage of the EC molecule and three examples are illustrated in Figs. 3C, 3D and 3E.

2.3 Derivatives Formed during Ageing of DPA- and EC-Stabilized Propellants

As discussed in Section 2.1, stabilizers act as nitrogen oxides scavengers. We should now consider two important issues on which surveillance programmes involving chemical analysis of residual stabilizers rely. These are which derivatives are expected to be produced and what is their order of appearance.

In order to answer the first question some authors have undertaken studies involving the chemical reaction of N₂O₄ with DPA (12) and EC (13) as well as the reaction of EC with HNO₃ (14) and HNO₂ (15). Afterwards, the chemical mixtures were analyzed by thin layer chromatography (TLC) in order to identify the products formed during the course of the reactions. Although, these experiments cannot be directly related to ageing processes which occur in gun propellants some interesting observations can still be made from the results obtained.

For DPA, the reactions involve nitration and nitrosation. The nitroso (-NO) group is always attached to the amine nitrogen (N-nitroso) and no C-nitroso derivatives

are formed. For the nitration, it appears that only C-nitro derivatives are formed and no N-nitro are formed. Furthermore, the nitro substitution appears to occur only at positions 2, 4 or 6 of the phenyl groups (ortho and para) and there is no formation of derivatives substituted in positions 3 or 5 of the phenyl groups (meta). This latter observation is quite understandable if one considers that the amine group in DPA is an activating ortho/para director relative to electrophilic substitution on the phenyl group.

With regard to EC, the reactions involved besides nitration and nitrosation are the cleavage of EC to form monoaromatic derivatives. In the process, only C-nitro derivatives of EC are formed, while for monoaromatic derivatives N-nitroso and C-nitro derivatives are formed. In all cases only ortho/para substitutions are observed due to the activating ortho/para director effect of the amide (or amine for monoaromatics) group relative to the electrophilic substitution on the phenyl group.

However, as stated above, these studies cannot be directly related to ageing processes which occur in gun propellants, nevertheless, several studies (10, 11, 16-29) have considered this issue. The exhaustive work of Volk (28, 29) will be used to discuss the results obtained.

Volk studied various DPA and EC stabilized propellants which had undergone artificial ageing between 65-90 °C and were sampled and analyzed by thin layer chromatography at regular intervals. The work of Volk was based on 30 possible derivatives of DPA and 25 possible derivatives for EC. Obviously, these included almost all possible derivatives. This study confirmed the above observations concerning the formation of N-nitroso and nitro derivatives with a preference for ortho/para substitutions. Moreover and above all, the study has showed that the formation of the various derivatives is sequential. As shown in Fig. 4, for DPA

stabilized propellants, N-nitroso and mononitro derivatives were among the first to appear and with increased ageing there are increasing degrees of nitro substitutions from mononitro to dinitro to trinitro and so on. The reaction scheme, for EC-stabilized propellants, is illustrated in Fig. 5. For these propellants, the formation of mononitro derivatives of EC is concomitant to the formation of mononitro or mono N-nitroso monoaromatic derivatives due to the cleavage of the original urea. With increased ageing, there are increasing degrees of nitro substitutions for EC and monoaromatic derivatives. A quantitative way to illustrate the sequential process is to plot the concentration of derivatives as a function of time of ageing (10, 11, 20, 23, 24-27, 30-32). Two examples are given in Fig. 6 (10) for a DPA-stabilized propellant and in Fig. 7 (11) for an EC-stabilized propellant.

As observed in Fig. 6A, as the concentration of DPA decreases the concentration of N-NO-DPA increases and reaches its maximum when the DPA is almost depleted (Fig. 6B). At the same time, mononitro derivatives of DPA (2-NO₂ and 4-NO₂) and the mononitro derivative of N-NO-DPA (N-NO-4-NO₂-DPA) increase in concentration and reach their maximum at about 10 and 20 days, respectively, and these derivatives are subsequently exhausted before 50 days. The dinitro derivatives of DPA (2,4'-di-NO₂, 4,4'-di-NO₂ and 2,2'-di-NO₂) appear between 5 and 8 days and reach their maximum between 30 and 40 days, and are exhausted before 90 days. The same pattern continues to apply for higher nitro derivatives, as illustrated in Fig. 6B. The same sequence is illustrated in Fig. 7 for an EC-stabilized propellant; as the concentration of EC decreases, the concentration of the mononitro derivative of EC (4-NO₂-EC) increases and reaches its maximum in about 12 days. At the same time, the cleavage of EC produces N-NO-N-ethylaniline followed by the appearance of higher nitro derivatives of EC or monoaromatics. As observed in Figs. 6 and 7, not all derivatives are formed at the same time thus, an analysis of the state of nitration of the stabilizer gives an idea of the extent of degradation. In others words, the determination

of the state of the stabilizer and its daughter products in any given sample of powder will give information about the history of this powder and an indication by which to assess its remaining "safe life". On the other hand, the exact mechanism by which the stabilizer derivatives are formed and the kinetics of their formation are, by no means, known with certainty, although there is considerable speculation in the literature (10, 11, 14, 15, 18, 20, 23, 33-37).

This is an understandable situation if one takes into account the complexity of the system. First, we are dealing with an heterogeneous medium where a solid phase (the powder) is interacting with a gaseous phase. Besides this macroscopic heterogeneity there is also a molecular intrastructural inhomogeneity. For instance, the individual NC molecules vary in size and composition and may even contain small quantities of impurities whose effect on the ageing process is unknown. The individual segments vary; in some, all the OH groups are replaced with nitrate groups, while others contain both kinds of groups and some have no nitrate group at all. In addition, the methods used in the preparation of the propellant and the gelatinizing agents introduce variation in the grain porosity which is an important parameter for the gas diffusion process. The geometry of the propellant (number of perforation, web size) has an effect on gas diffusion similar to that of grain porosity. All these factors have proven to influence the rate of nitrate ester decomposition and the chemical reaction schemes (8, 33, 38, 39). The succession of reactions can also be affected by several others factors. For instance, certain ingredients, such as ballistic modifiers (40), plasticizers (23, 41) and calcium carbonate (38, 42, 43) which are added to propellant formulations can influence the ageing process. In addition, environmental factors such as water content, temperature cycling, humidity conditions during storage and oxygen concentration have been shown to have a definite influence on the ageing process (32, 38, 42, 44, 45).

Furthermore, the mechanisms of formation of the derivatives are not definitely proven. For instance, for EC-stabilized propellants the formation of monoaromatic compounds may proceed through different paths (11, 15, 18, 20) and the ratio of monoaromatic to urea products increased as a function of EC level (20). For DPA-stabilized propellants, the Fisher-Hopp reaction, which is often mentioned for the transformation of N-nitroso derivatives to C-nitro derivatives, has been judiciously noted by Curtis (23) to require the presence of chloride or bromide counter ions which are not added to most gun propellant formulations. It has been shown that the relative amount of derivatives changes according to propellant type (23). There are also several speculations about the reaction scheme for N-nitroso DPA and this issue will be discussed in more detail in Section 5.3. Finally, it has also been shown (10, 11, 16, 20) that the summation of concentrations of daughter products, corrected for molecular weight changes, never accounts for 100% of the original level of stabilizer. This means that the stabilizer and maybe some derivatives, are likely involved in reactions other than those described above, for example the stabilizer can become covalently bonded to the NC and therefore it is not extracted.

As discussed above, several factors could influence the ageing process and for more details the aforementioned references and a previous DREV report on DAME task 73 (38, 46, 47) should be consulted. Consequently, there is not a definite and universal way by which propellants age. Therefore, graphs such as Figs. 6 and 7 are valid only for the propellant studied. The derivatives formed and the proportion of each one might change significantly from one propellant to another or even from lot to lot of the same propellant. Of course, higher nitro derivatives will not appear before lower nitro derivatives and not all derivatives will be found in a powder. Nevertheless, the ones that would be found will be among those discussed above and will appear in a sequential way as described in Figs. 4 and 5. The older the propellant, the higher will be the level of nitro substitution on the stabilizer. This important fact was

confirmed by all the aforementioned studies. Consequently, the determination of the state of the stabilizer and its daughter products in any given sample of powder will give information about the history of this powder and an indication of its future usefulness. In others words, the determination of stabilizer and its reaction products give a quick snapshot of the propellant stability. The speed at which a given propellant will degrade is dependant on many variables, as discussed above, and this is the reason why periodic monitoring of propellant stability is so important.

Before closing this chapter we would like to mention, at this point, that the degradation of NC does not consist only of the splitting off of the nitrate ester groups but also of a breaking of the cellulose chains as a result of various consecutive oxidation reactions which also produce gases which are insoluble in the matrix and invariably lead to cracking. As a consequence, concomitant to chemical ageing there is a mechanical and ballistic ageing and these processes are interdependent. Degradation of mechanical properties is often a decisive factor in determining the storage life of rocket motors but since the scope of this work is chemical ageing we will not go into details concerning the mechanical and ballistic ageing and further information on this subject can be found in the following work (48-54) and the references therein.

3.0 GUN PROPELLANT STABILITY TESTING

As discussed in the previous chapter, even at room temperature, propellants will degrade upon storage. The addition of chemical stabilizers such as, DPA or EC, can increase the lifetime of propellants by reacting with the nitrogen oxides and thereby delay autocatalysis. In order to determine the extent of the degradation of propellants and then to assess their stability, some physical or chemical property of the propellant is monitored. A large number of different surveillance tests for the sentencing of

propellants have been developed over the years. Some of them have been used for a long time and are referred to as the traditional tests while others were developed recently and are referred to as modern tests. In this chapter, we will first discuss briefly the different methods available to monitor gun propellant stability. Secondly, we will describe the current CF gun propellants surveillance programme and its weaknesses. Finally, we will propose a new surveillance programme based on HPLC and discuss the rationale behind this choice.

3.1 Classification of the Methods of Monitoring Gunpowder Chemical Stability

Several propellant properties may be used to assess its stability. The methods can be classified into the following categories (55): production of oxides of nitrogen, spectroscopic properties of NC, molecular weight of NC, heat evolution and stabilizer analysis.

3.1.1 Production of Oxides of Nitrogen

Most of these methods date back to the beginning of this century and are purely empirical. In these tests the propellant is heated at a specific temperature and the nitrogen oxides produced (mainly NO_2 and NO) are monitored. For the Abel heat test, the methyl violet paper test and the Vieille test, the detection of nitrogen oxides is done with specially treated paper which changes colour in presence of nitrogen oxides (38, 56). The propellants are sentenced according to the time it takes for the paper to change colour. For the Bergmann and Junk test and potentiometry (56) the evolved gases are dissolved in water and the acid formed is titrated and this latter result is used for sentencing. In some other tests, such as the Dutch test (56), the propellant is heated in an open test tube where the volatiles are allowed to escape and the loss in weight is used to evaluate the stability of the propellant. Chemiluminescence has been used

to monitor the evolution of nitrogen oxides (57-60). This modern method is a powerful tool in the study of propellant decomposition but, on the other hand, chemiluminescence does not provide sufficient information to make sound predictions about the future behaviour of a propellant.

3.1.2 Spectroscopic Properties of NC

NMR and IR have been used to characterize propellants. However, for both techniques, no significant differences have been found between the spectra of freshly manufactured single-base propellant and a sample aged at 80°C or ambient temperature over at least ten years (61). It may thus be concluded that these spectroscopic methods are not useful for stability measurement.

3.1.3 Molecular Weight of NC

Gel permeation chromatography (GPC) can be used to follow the reduction in molecular weight of NC which occurs concomitantly with its degradation. It has been shown that molecular weight and mechanical properties correlate well with stabilizer degradation (49). For surveillance use however, this method suffers a lack of precision since the molecular weight observed is dependant on various factors such as the source of NC, manufacturing methods and sample preparation techniques. Therefore, it is difficult to assess sentencing criteria based on this method. Nevertheless, GPC is a useful technique to study stabilizer effectiveness (62, 63).

3.1.4 Heat Evolution

A technique that has raised considerable interest during the last fifteen years is microcalorimetry. This technique measures the heat flow from the exothermal

reactions involved in nitrate ester degradation. One application of this method is to measure the heat generation of a propellant at a specific temperature (isothermal heat generation). Isothermal heat generation has been used to give information about self ignition hazards (64-66) and to determine the critical diameter, i.e. the smallest diameter at which self-ignition takes place (66). For instance, using such a method and a mathematical model the French (67) have shown that for a specific single-base powder, a high value of heat generation must be reached to yield to self-ignition in a 30-mm caliber. Indeed, according to this study, for calibers of 30 mm or less, there is virtually no risk of self-ignition even with a degraded powder. On the other hand, in a 150-mm munition, values between 100 and 150 mW/kg, i.e. values observed for degraded powder, can lead to self-ignition. Of course, the risk of autoignition is even greater in bulk storage since, in this case, heat generation of as low as 15 mW/kg can result in autoignition. The French use microcalorimetry as the final method to double check propellants that were sentenced hazardous by chromatographic methods. In the Netherlands, a method was developed (68) which enables a rapid and accurate determination of the effective stabilizer content in propellant. However, the strong influence of environmental conditions emphasizes that a comparison between experiments is only acceptable if similar conditions are used in the experiments (32).

Despite the fact that microcalorimetry is used as part of the surveillance programme in France, the Netherlands and Sweden, there is a high capital equipment cost associated with this test and another drawback of this technique from the quality assurance point of view, is that the apparatus cannot easily be adapted to handle a large number of samples. Nevertheless, this technique is complementary to chromatographic techniques and we suggest that the CF consider this method in the future for the evaluation of the risk of self-ignition of those powders that would have been sentenced hazardous according to chromatographic techniques.

3.1.5 Stabilizer Analysis

Stabilizer analysis can be divided into two types of methods. The classical one involves wet chemistry and spectrophotometry and the second class consists of methods based on chromatography.

The classical and older methods involve digestion, extraction or steam distillation to extract the stabilizer which is then quantified either by spectroscopy (69-71), volumetric bromination (72-78) or gravimetric determination (79, 80). Among these methods there is the colour test (81, 82) which is used for EC-stabilized propellants. The colour test involves the comparison of an acetone solution of the propellant with a standard solution in order to assign a colour number by which the chemical stability of the propellant can be assessed. This method will be discussed later since it is used in the current CF gun propellant surveillance programme (82). However, these classical methods are cumbersome, time-consuming and moreover, lack specificity since in many instances not only the stabilizer is measured but also its primary degradation products. As a consequence, these methods have been replaced over time by more modern analytical methods based on chromatography.

The first studies which gave a more thorough insight into gun propellant ageing involved column chromatography (10, 11, 83). In fact, these studies were among the first ones which enabled the separation and the quantification of the stabilizer as well as its reaction products. However, identification, separation and quantification of each of the products by column chromatography is tedious, requires large quantities of solvent and is time-consuming, so most researchers turned their efforts toward more modern methods such as thin layer chromatography (TLC) (12, 13, 27-29, 84-92), gas chromatography (GC) (93-97) or high-performance liquid chromatography (HPLC) (16, 17, 19-22, 26, 27, 95, 97-117).

It appears, from this discussion, that methods such as TLC, GC and HPLC are among the best for monitoring the chemical stability of gun propellants. In fact, these methods have been used for several years in several countries for gun propellant stability surveillance programmes. However, the current CF gun propellants surveillance programme is still based on spectrophotometric or production of nitrogen oxides methods which, according to past experience, have some shortcomings.

3.2 The Current Canadian Gun Propellants Stability Surveillance Programme

Propellants stored in bulk (prior to filling) or in ammunition are among the biggest items in the DND inventory and an effective surveillance and testing programme is essential for the maintenance of safety and the maximum use of resources. The current surveillance and testing programme in the CF is done according to the CFTO-C-74-300-C01/NB-000 (82). In accordance with this technical note, most gun propellants used by the CF, a list of which is given in Tables I and II, must be tested by the Abel heat test (Part 3, Ref. 82) and those stabilized with EC may also be tested by means of the colour test (Part, 4 Ref. 82).

The Abel heat test is based on the principle that when a sample of the propellant is heated (65.6 °C or 71 °C according to the propellant), oxides of nitrogen are liberated more or less rapidly according to the stability of the material. These oxides of nitrogen are detected by means of a starch-potassium iodide test paper of which the upper half is wetted immediately before use with a mixture of glycerine and water. During the test, the junction of the wet and dry halves of the paper assumes a brownish tint which gradually deepens and the test is completed when this tint matches that of a standard tint paper. The time taken to reach the standard tint is used for sentencing the propellant according to the criteria given in Tables 4.5 to 4.13 of Ref. 82.

The colour test is used in special cases where the propellant is stabilized with EC and does not contain coloured ingredients. It is a qualitative measure of the amount of EC derivatives produced in the propellant since they produce a coloured solution when the propellant is dissolved in acetone. The intensity of the colour of this solution is compared with those of various standard ammonium cobalt (II) sulphate/potassium dichromate solutions. The results from this comparison determine a colour number which is used to sentence the propellant in accordance with the criteria found in Tables 4-5 to 4.13 of Ref. 82.

If a propellant fails these tests, it is sent to National Defence laboratory facilities to undergo analysis via the STANAG 4117 method. This is the NATO procedure and involves the digestion of the propellant with hot ethanolic sodium hydroxide solution followed by steam distillation of the resultant mixture and finally spectrophotometrical examination of the distillate. The result is expressed in terms of effective stabilizer.

However, this testing programme has several drawbacks. For instance, the Abel heat test is influenced by several variables such as the moisture content, interference of impurities, difficulties in ascertaining the end point and so on (118, 119). These factors are largely responsible for the erratic results. In fact, there are several examples in the past where the Abel heat test gave a false alarm, that is, a propellant was sentenced unstable while it was actually stable (38, 120). Moreover, the inverse situation, that is, an unstable propellant sentenced as stable has also occurred (121). This latter situation is very dangerous and it precludes the use of the Abel heat test for routine analysis of aged propellant, especially for the sake of reliability and security.

The colour test applies only to EC-stabilized propellants which do not contain coloured ingredients or impurities thus, this is not an universal test and consequently

a relationship between the residual EC and the colour number should be determined for each new EC-stabilized propellant. The determination of colour number is done by visual comparison and the result may change depending on the operator, although, the Australians have developed (122) an improved test based on spectrophotometric determination. Nevertheless, despite its relative simplicity this test is still non universal, qualitative and unreliable since it is not obvious which species, the stabilizer derivatives or coloured impurities, are primarily responsible for the yellow of the acetone solution.

The STANAG 4117 method, as mentioned above, is tedious, time-consuming and lacks specificity since the nitroso derivatives are changed back to the parent stabilizer and contribute to the result as well as the lower nitrated derivatives which are volatile in the steam.

It is clear that the current surveillance testing has some shortcomings. Moreover, the present equipment in Canadian depots is old and in need of replacement. Furthermore, improvements in analytical techniques and a deeper understanding of the chemistry of the degradation process have opened the door to the replacement of these older methods with more modern ones. Consequently the time has come to change the current programme for a modern, reliable and efficient programme that will allow a more precise estimate of the remaining safe life of a propellant lot.

3.3 Proposal for a New Surveillance Programme

The first studies using chromatography involve column chromatography (10, 11, 83). However, since column chromatography is a tedious technique, TLC has rapidly replaced it. The earlier studies involving TLC showed excellent separation of

stabilizer and daughter products. TLC was used in two methods developed at DREV for single base(88, 96) and for double- and triple-base propellant (87). However, it is difficult to quantify the products with TLC and consequently to assess sentencing criteria. Moreover, TLC is a slower method that does not lend itself to automation. Nevertheless, recently considerable progress has been made in TLC (89, 90, 123) but to the best of the authors' knowledge, this technique is not accepted worldwide unlike GC or HPLC for the routine analysis of aged propellant. In fact, in USA(21, 124), France (125), the UK (126) and Australia (127), GC and/or HPLC are used for the gun propellant stability surveillance programme.

However, one drawback to GC is the thermal stress placed on the products in order to volatilize them. Indeed, the nitroso derivatives are thermally unstable and therefore, GC is limited by its inability to separate DPA and N-NO-DPA which is converted back to DPA. It is important to quantify N-NO-DPA since it is a stabilizer and is included in the level of effective stabilizer which is used for sentencing the DPA-stabilized propellants. This is why in countries that use GC and HPLC the former is used firstly to screen the propellant but when the level of DPA reaches a certain limit, HPLC, which does not impose a thermal stress, is used in order to discriminate between DPA and N-NO-DPA. On the other hand, HPLC is slower than GC and therefore, has higher running costs and lower sample throughput. However, the number of samples tested in Canada was determined to be about 200, much lower than the number of samples tested in countries like USA, UK or France. Consequently, this reduces the sample throughput and running cost drawbacks of HPLC. Furthermore, the next issue of NATO STANAG 4117 will include an HPLC alternative to the spectrophotometric method but GC will not be included for the reason mentioned above. Consequently, because there is no restriction on the use of HPLC and since this method has been selected by the NATO countries, we have

decided to select this widely accepted method for implantation into a new Canadian gun propellant stability programme.

4.0 DEVELOPMENT OF HPLC METHODS

4.1 Introduction

As discussed in Section 2.3 the level of nitration of the stabilizer is an indication of the state of ageing of any gun propellant sample. HPLC, because its capability to resolve many components in a mixture, was selected for monitoring the stability of gunpowders used by the CF, the gunpowder being either DPA-stabilized or EC-stabilized. Therefore, the aim of the present work is to develop or find in the literature an HPLC method that can give an adequate picture of the state of ageing of DPA-stabilized gunpowders and another method for EC-stabilized propellants. At this point, it must be stressed that the objective of this work was not to develop exhaustive and research grade methods that produce a baseline separation of all the possible products; such methods have already been developed in Australia by Curtis et al. (16, 20). Instead, our objective is to develop methods that can be used on a routine basis and probably by personnel not necessarily having the chemist's knowledge of HPLC. Therefore, the objective of this work was to develop methods that can be used routinely and that are efficient, fast and reliable.

First, in order to give an adequate picture of the state of ageing of a given sample of gunpowder, the methods must sufficiently resolve the stabilizer as well as its daughter products. In addition, the method must consider the other ingredients in the powder that could interfere with the stabilizer and its derivatives. Thus, the efficient methods are those that take into account all the possible products that either

are present or that can be produced during the ageing process of the gunpowder formulations used by the CF.

Secondly, as discussed in Section 3.3, one drawback of HPLC is its low sample throughput. So, in order to minimize this disadvantage the methods should be not only able to separate the various components adequately but they should also do it in the minimum time possible without much loss in resolution.

Thirdly, for the sake of reliability, the methods should be developed for bonded phase silica columns as opposed to unmodified silica columns. In fact, the former are generally viewed as superior to the latter in terms of reproducibility (128). Unmodified silica columns are less popular because of problems in maintaining a constant surface activity required for repeatable separation. For instance, retention with unmodified silica columns is more inconsistent because of their sensitivity to small concentrations of water in the sample or in the mobile phase (129). Among the various types of bonded phase silica columns, there are the reverse phase columns which are the most popular (130) primarily because of advantages such as short equilibrium time, separating capability for polar as well as non-polar solutes and good reproducibility of retention times.

Finally, these methods used for routine analysis of aged propellants, and according to our experience, the most appropriate methods are those using isocratic mobile phase as opposed to a mobile phase gradient. The next step is to search in the literature for methods that meet the aforementioned criteria.

According to the discussion in Subsection 3.1.5 regarding HPLC, many investigators have reported on the HPLC analysis of DPA, EC and their reaction products. However, in our opinion, none of these methods fulfilled the above-

mentioned requirements. In fact, many of these methods either considered a limited number of derivatives or are sparse in detail regarding the other ingredients that are present in the gun propellant formulations used by the CF. On the other hand, the methods that are adequate in terms of the products considered either use unmodified silica columns, take more than 30 minutes for each sample or use gradient elution. Consequently, it was decided to develop new methods to meet the above-defined requirements. However, before going any further in the development work, and in order to meet our first requirement, we must have a knowledge of all products requiring separation.

4.2 Products to Consider for HPLC Separation

Our first requirement is that methods should adequately separate the stabilizer, its daughter products and the ingredients used in the gunpowder formulations.

The daughter products that can be produced during the ageing of DPA- or EC-stabilized gunpowders have already been discussed in Section 2.3. A large number of degradation products have been considered in the various studies referenced in Section 2.3. However, the rationale behind the choice of a particular product is not always clear. For instance, some authors considered C-NO₂ derivatives of DPA or EC substituted in position 3. Such substitution are unlikely to appear according to the discussion in Section 2.3 and, in fact, these derivatives were not observed in the analyses of aged gunpowders. Furthermore, the situation is even more confusing for the derivatives formed after extensive ageing. For instance, in EC-stabilized powder, some authors considered the nitrophenol and nitrobenzene derivatives, while others considered derivatives such as the 1-ethyl-3-(4-nitrophenyl) 1-urea (i.e. lost of an ethyl group from 4-NO₂-EC). However, in our opinion, we must distinguish between the degradation products expected and those really produced during ageing. In other word,

even if several possible degradation products of DPA and EC have been investigated, not all of them have been observed while some others are produced to a very low extent. Therefore, in this work, for the sake of completeness and precision as many degradation products as possible have been considered.

A list of the degradation products for DPA-stabilized powders is given in Table III. This list contains almost all the products considered in the references of Section 2.3. It includes also the 2,3,4,6 tetranitro DPA derivative. This is in contradiction with the Section 2.3 where it was stated that substitution in position 3 is unlikely. On the other hand, the upgraded version of STANAG 4117 included, probably erroneously, this derivative in the list of the main degradation products. Therefore, this derivative was included in Table III in order that the DPA HPLC method conform to STANAG 4117.

The list of degradation products for EC-stabilized powders is given in Table IV. As for DPA, as many degradation products as possible are considered. However, the derivatives produced after extensive ageing such as nitrophenol, nitroaniline and degradation products consisting of the lost of the ethyl group from EC or 4-NO₂-EC have not been considered. This is because in the studies referenced in Section 2.3 these degradation products are either not observed or observed only after a long period of heating at temperature as high as 80 °C. Therefore, these products are unlikely to be produced during normal storage temperature. Nevertheless, those products which were available at DREV were included in Table IV, while the purchase or the synthesis of the others were not worth the expense for the above-mentioned reasons.

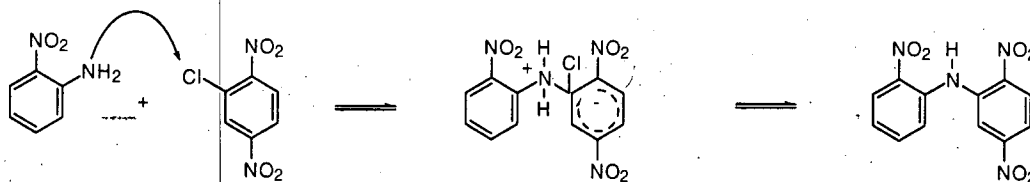
In addition to the degradation products of EC and DPA, the gunpowder formulations also contain ingredients such as plasticizers, burning rate modifiers, etc. We will now discuss which of these ingredients must be considered .

Gunpowders are mixtures of organic ingredients such as NC and inorganic ingredients such as potassium sulphate. As we will see later, the powder, prior to HPLC analysis, is dissolved in acetonitrile (ACN) and a small amount of a 2% CaCl_2 solution is added to precipitate the NC, in order to eliminate it from the solution to be analyzed. The inorganic ingredients such as K_2SO_4 , KNO_3 , graphite, CaCO_3 , Na_2SO_4 , $\text{Ba}(\text{NO}_3)_2$ etc. are not soluble in this solvent and, consequently, these ingredients will not interfere in the subsequent HPLC analysis. On the other hand, organic ingredients are soluble in this solvent mixture and therefore may interfere in the subsequent HPLC analysis. In order to establish which powder ingredients must be considered to develop a suitable method, a list of gunpowders used and stocked in the Canadian magazines was provided by DACME (131, 132). The formulations of DPA-stabilized powders are given in Table I and those for EC-stabilized powders in Table II. For the above-mentioned reason, the inorganic ingredients have been excluded in Tables I and II. According to Table I, in order to develop an HPLC method for DPA-stabilized powders, the products that should be considered, in addition to the daughter products given in Table III, are: dibutylphthalate (DBP), diethylphthalate (DEP), diphenylphthalate (DPP), dinitrotoluene (DNT) and nitroglycerine (NG). For the EC method, in addition to the daughter products given in Table IV, the following products, according to Table II, should also be included: n-butylstearate (NBS), camphor, diethylphthalate (DEP), diphenylphthalate (DPP), nitroglycerine (NG) and nitroguanidine (NQ).

4.3 Synthesis of DPA and EC Derivatives

Very few of the daughter products of DPA and EC discussed in the previous section are commercially available. Therefore, all the synthesis was contracted to Omega Chemical Company Inc. (Lévis, Québec, Canada). In this section, details regarding the synthesis will be given.

The nitro-DPA derivatives were synthesized by the condensation route between a nitro-substituted aniline with a nitro substituted chlorobenzene. The synthesis of 2,2',4-trinitro-DPA from 2-nitroaniline and 2,4 dinitrochlorobenzene illustrates this condensation route:



This type of reaction has been well studied and thorough details and discussions are given in Ref. 133.

Two DPA derivatives, 2,2'-dinitro-DPA and 2,4'-dinitro-DPA will be used for mobile phase adjustments, as will be discussed in Section 4.4. These two products are either difficult to find commercially or very expensive and therefore their synthesis will be given in detail.

The 2,2' isomer was prepared as follows (133): 2-nitroaniline (2.76 g., 0.02 mol.) and 2-chloronitrobenzene (1.58 g., 0.01 mol.) were heated to reflux in 20 ml DMF. Potassium carbonate (1.38 g., 0.01 mol.) was added and the mixture heated for a further 24 hours. The cooled reaction mixture was washed into 500 ml of rapidly stirred 1 M HCl with ethanol and the product collected by filtration. The crude product was further purified by dissolution in 200 ml dichloromethane and washed with 1 M HCl (3 x 200 ml) and water. The dried and evaporated residue was decolorized with carbon in 100 ml acetone and precipitated by the addition of 400 ml water to the filtrate. Recrystallisation from 35 ml of boiling 1:1 ethanol/acetone gave 1.02 g. of the product (m.p. 171-2°, lit. 172° (10)).

The 2,4' isomer was prepared according to a method that is similar to the one above, from 2-nitroaniline and 4-chloronitrobenzene in DMSO (90 min.) reflux. The lower solubility of the 2,4' isomer required that the decolorizing be carried out in 200 ml acetone and the product reclaimed by the addition of 4-volume water. This yielded red fluffy needles after recrystallisation from about 60 ml acetic acid 1.3 g.(50%) (m.p.222-223 °C, lit. 224-224.5 °C (10)).

The nitroso derivatives of DPA were synthesized either by the nitrosation of the corresponding nitro derivatives or by nitration of N-nitroso derivatives, all the details are given in Ref. 23.

Some monoaromatic derivatives of EC are commercially available from Aldrich. The synthesis of those not commercially available as well as the urea EC derivatives are described in detail in the following references (14, 15, 134-136).

The purity of the synthesized derivatives was first checked by HPLC in order to verify if only one peak was observed. Afterwards, its melting point was determined and compared with those found in the literature (14, 15, 23, 33, 34, 135-137). The UV spectrum as well as the IR spectrum were also compared when available in the literature (135, 137). All the melting points, the UV spectra and the IR spectra were recorded and all this information will be published shortly in a DREV memorandum.

Finally, it must be mentioned that the di-nitro N-nitroso DPA derivatives and the 2,2',4,4',6 penta-nitro-DPA decompose upon storage. The N-ethyl-2-nitro-N-nitrosoaniline did not give a single peak in HPLC. This compound gave rise to double peaks without baseline separation, which produced a single peak as the column temperature rose. The same observations have been reported previously (20) for the

same EC derivative and this behaviour is probably caused by an equilibrium between two forms of the product.

4.4 HPLC Method for DPA-Stabilized Propellants

The development of an HPLC method follows well-defined steps as discussed in Refs. 138-141. Drylab I/plus software was used to assist and facilitate this task. The aim was to develop an efficient, fast and reliable method that must consider the products of Table III and the following ingredients : DBP, DAP, DPP, DNT and NG. However, with such an exhaustive list of products to be considered it is almost impossible to meet the requirements of minimum run time with an isocratic elution. On the other hand, as we will see later, the sentencing criteria in most countries are based on the effective stabilizer which is the summation of the concentration of DPA and the concentration of N-NO-DPA. Consequently, it does not worth the effort of trying to obtain baseline resolution for each compound and our first requirement should now be the development of a method that can separate DPA and N-NO-DPA from any interference from all other possible products that can be present or produced during the ageing of a gunpowder stabilized with DPA.

The first trial was done with the binary mobile phase ACN/water. The results obtained are summarized and illustrated in Figs. 8 and 9. Figures 8 and 9 are resolution maps which are plot of percentage of organic versus the resolution of the critical pairs. The critical pair is the pair of peaks that is the least resolved for any mobile phase concentration. For instance, Fig. 8 is the resolution map for N-NO-DPA and as observed the maximum resolution is about 1.1 at about 71% of ACN and the critical pair is 2,4' DNDPA/N-NO-DPA on the left and 2,2' DNDPA/N-NO-DPA on the right. Figure 9 is the resolution map for DPA and as illustrated at 71% ACN the resolution is about 1.2 and the critical pair is 2,4 DNDPA/DPA. In order to increase

our resolution, the MeOH/water mobile phase was tried. However, for a run time of less than 20 minutes it was impossible to separate adequately DPA and N-NO-DPA from the di-NO₂-DPA derivatives. Some di-NO₂-DPA coeluted with DPA and N-NO-DPA and, moreover, the pressure was higher than that observed for the ACN/water mobile phase. Even if the run time was sacrificed (run time > 20 min.) it was not possible to obtain a method giving adequate separation for DPA or N-NO-DPA. For instance, under the best conditions, the MeOH/water mobile phase does not succeed in adequately separating N-NO-DPA. Indeed, N-NO-DPA was coeluting with a tri-NO₂-DPA derivative (2,4,4'-TNDPA).

In this work, the THF/water mobile phase was not tried because this solvent is unpleasant to work with, tends to form explosive peroxides and is more difficult to flush from the LC system than the other solvents. Consequently, all these drawbacks preclude the use of THF for a routine method. A tertiary mobile phase, ACN/MeOH/water was also tried and slightly better resolutions ($R_s \approx 1.5$) for DPA and N-NO-DPA were obtained but at the expense of the run time which exceeded 35 minutes. The latter method costs more in terms of solvent and sample throughout (i.e. 35 minutes instead of 15 minutes). On the other hand, the ACN/water meets our requirements and this is an excellent routine method. Its resolution is slightly lower than the tertiary mobile phase method, but as will be discussed below, this is not a real drawback for a surveillance programme.

Therefore, the ACN/water method was selected and after optimization of the column length, packing particle diameter, mobile phase flow rate and column temperature, the best separation was obtained with the conditions given in Table V. Table VI gives the retention times obtained with this method for all the products considered. Figure 10 is a chromatogram obtained with this method for the first ten derivatives of DPA. As discussed above, the ACN/water method was preferred to the

ACN/MeOH/water method because of its better sample throughput and lower consumption of solvent, but this choice was done at the expense of the resolution. However, in the case of a surveillance programme, this is not a real drawback. This can be illustrated with the artificial ageing at 65.5°C of an DPA-stabilized single base gunpowder (FNH) where samples were analyzed by the ACN/water DPA method at specific time intervals. The chromatogram obtained for the original and 90, 120 and 180 days aged samples are illustrated in Fig. 11. The height of the internal standard (EC) is constant for these four figures. According to its relative height to EC, it appears that DPA decreases with heating time and that it is almost exhausted at about 120 days. On the other hand, the concentration of N-NO-DPA increases with heating time, reaches a maximum at about 120 days and decreases afterwards. This behaviour is typical of the sequential ageing process as discussed in Section 2.3. Moreover, this example illustrates that the lower resolution for the method compared with the tertiary mobile phase method (ACN/MeOH/water) is not a drawback. In fact, as discussed above for the DPA method the critical pairs are 2,4'-di-NO₂-DPA/N-NO-DPA and 2,4-di-NO₂-DPA/DPA, but the di-NO₂-DPA derivatives are not produced at the beginning of ageing process and when they are produced (at about 120 days) at this stage of ageing there is no more DPA and consequently, as we will see later, the concentration of effective stabilizer will be too low and the powder will not pass the sentencing criteria and will be considered dangerous in terms of autoignition. Nevertheless, as illustrated in Fig. 10, the resolution for the critical pairs 2,4'-di-NO₂-DPA/N-NO-DPA is still acceptable for quantification purposes, while the resolution for the 2,4-di-NO₂-DPA/DPA critical pairs is not a real problem since, even when DPA is almost depleted, the 2,4-di-NO₂-DPA is produced, if so, to a very low extent. Furthermore, it must be pointed, as discussed in Section 2.3, that the summation of concentrations of daughter products, corrected for molecular weight changes, never accounts for 100% of the original level of stabilizer. Actually, as the ageing process advances this summation deviates more from 100%. This explains that the derivatives that are

produced to a significant extent are the first ones such as N-NO-DPA and mononitro-DPA, while the more nitrated derivatives are produced in lower concentrations. Actually, if any trinitro or higher nitrated derivatives are formed it will probably be at a such level that they will be almost lost in the noise level of the baseline. This important observation means that a method could have been developed with only the following derivatives of DPA: N-NO-DPA, mono-nitro DPA, mononitro-N-nitroso DPA and di-NO₂-DPA. However, for the sake of completeness, precision and in the eventuality that higher nitrated derivatives could be produced to a significant extend, we did not take any chance and decided to develop a method that considers as many daughter products as possible.

The last example shows that the DPA method works well with single-base powders. In fact, DPA and N-NO-DPA, the two products that will be considered in our sentencing criteria, are well resolved and free of any interference from any other DPA daughter products. Other ingredients such as DNT and DBP give peaks well separated from the products of interest. At this point, we would like to point out that even if DBP has a long retention time (~ 23 min. in Table VI), it is possible to keep the analysis time down to 15 minutes. Indeed, the analysis will be done in series, so by careful adjustment of injection times the peak for DBP will elute near the beginning of the chromatogram for the next sample. This is illustrated in Figs. 11B, 11C and 11D which were recorded in series so that the DBP of sample B gives rise to a peak at about 4 min. on chromatogram C and the DBP of sample C gives rise to a peak at about 4 min. on chromatogram D.

At this point, the problems related to retention should be discussed. In HPLC retention is a function of the mobile phase strength and the stationary phase (the column). Once a method is developed with a given column, the mobile phase never changes and therefore the retention time should not change with time. However, as

the HPLC column ages it loses some of its original properties. This is due to the deterioration of the packing as a result of changes in the organic stationary phase, absorption of strongly retained impurities, etc. These changes in the stationary phase will consequently influence the retention. Therefore, retention time, as given in Table VI, should not be taken as absolute but as relative since they will change as the column ages and even from column to column. For example, Table VII illustrates how the retention times change as the column ages. The first column contains the retention times given in Table VI, i.e. retention times were determined when the column was almost new, while the second column contains the retention times obtained after one year of use of the column. The third column gives the ratio (between columns 1 and 2). As observed when the column ages the retention times shift in a regular manner. In other words, they do not jump randomly in the chromatogram. However, as illustrated in Table VII, as the column ages the retention times change and this could impair the resolution. Therefore, a periodic check of the column performance should be done to ensure the quality of the separation. This subject will be discussed in Section 4.9.

As discussed, the retention times are not absolute and moreover, as stated above, the retention might change from column to column despite the fact that the columns are from the same manufacturer. This is caused by changes in the various parameters involved in column preparation. For instance, the base silica particles and the reagents for the bonding process may come from different suppliers and this can introduce an impurity not present in previous column batches. The packing of the stationary phase into the column, the coverage by the stationary phase and several other variables can also affect the chemistry of the stationary phase. Consequently, no matter how carefully manufacturers prepare columns, there are differences between nominally identical columns. This variability between columns means that slight

adjustments in the mobile phase strength may be necessary to allow for column to column variation.

The procedure for these slight adjustments will be discussed. An interesting paper related to this topic is Ref. 142. As indicated in Figs. 8 and 9, the most critical pairs in the chromatogram of the DPA method were the 2,4'-di-NO-DPA/N-NO-DPA and 2,2'-di-NO₂-DPA/N-NO-DPA. Indeed, the resolution for the 2,4-di-NO₂-DPA/DPA pair was higher therefore this pair was not chosen. Hence, the procedure to compensate for column-to-column variation, consists in using a solution containing 2,4'-di-NO₂-DPA, 2,2'-di-NO₂-DPA and N-NO-DPA and, using this solution, elute it with the new column and different mobile phase strengths. The procedure is illustrated in Fig. 12 for three different mobile phase strengths. Figure 12 B is the nominal mobile phase composition as given in Table V of this work. As observed the resolution obtained with the new column is worse than the one we obtained with the previous column (see Fig. 10). Slight variations in the mobile phase composition (2% each side) were done and the resulting chromatograms are illustrated in Figs. 12A and 12C. As observed for this particular column, the resolution improves with the decreasing percentage of ACN. The next step would be to try 67% ACN and continue in a similar manner until a decrease in resolution is obtained and then work backwards until the maximum resolution is reached.

Of course, for this procedure, the same type of column, that is a Merck Lichrocart Superspher RP-18 end capped, 3 μ m, 25 cm X 4.6 mm column, was used. This is the best way to overcome the column to column reproducibility problem. Indeed, if a RP-18 end capped column from another supplier was used, differences in reagent sources, surface coverage by the stationary phase, silica characteristics and bonding techniques would result not in slight, but significant differences in retention and selectivity. For this reason, we strongly recommend buying columns packed with

the same batch of packing material. For instance, if a column last four months we recommend buying three columns at the time and to make sure they come from the same batch. Using columns with the same packing will greatly decrease the chance of encountering problems of retention caused by switching from one column to another. The following year, when a new column batch (same manufacturer, same part number) is purchased, it might be necessary to adjust the mobile phase composition as described above. A adjustment once a year should not imply a significant increase in workload.

4.5 Method for EC-Stabilized Propellants

In the HPLC method for EC-stabilized propellants, the goal is to separate the daughter products of EC given in Table IV and the following ingredients: n-butylstearate (NBS), camphor, diethylphthalate (DEP), diphenylphthalate (DPP), nitroglycerine (NG) and nitroguanidine (NQ). However, as described in the section regarding sentencing criteria, only the concentration of EC will be used. Consequently, the EC method must adequately separate EC from all the above-mentioned products. In addition, for economic and practical reasons, it would be worthwhile to use the same column and the same solvent as used for the DPA method. In fact, this will minimize solvent stockage and cost but, furthermore, if the same solvents are used, this will minimize the equilibration time when switching methods and, consequently, maximize the sample throughout.

In a similar way, as for the development of the DPA method, the binary mobile phase ACN/water was tested and fortunately proved to have very good resolution for EC. The optimized conditions are given in Table VIII, and the retention times for the list of products is given in Table IX. Figure 13 is a chromatogram obtained with this method for the major EC derivatives. As shown in Fig.13, the resolution for EC is

excellent that is, greater than 2 for the DPA/EC pair and greater than 4 for 2,4-di-NO₂-EC/EC pair. This is a rugged method that should not be affected greatly by column to column variation. However, for the sake of precision, the resolution between DPA and EC might be slightly adjusted but, in this case it is not imperative as it was the case for the DPA method. This adjustment can be done in the same way as described in Section 4.4 for the DPA method but using the EC/DPA pairs instead.

The EC method was applied for a double-base powder (AKB 204) aged artificially at 65.5°C. The chromatograms obtained for the original powder and 90 , 215 and 360 days aged samples are illustrated in Fig. 14. Again, in these chromatograms, the height of the DPA peak is constant and, as can be observed, the EC concentrations decrease as the ageing process advances. This example clearly demonstrates, again, that as the powder ages a lower percentage of the original stabilizers are recovered but, as in the case of DPA and for the sake of completeness and precision, we decided to develop a method that considers as many EC derivatives as possible.

Figure 15 shows the chromatograms obtained for a triple-base (SPCG) powder artificially aged at 65.5°C. The height of the internal standard DPA is constant in these four chromatograms. As observed, the triple-base powder aged very slowly. Even after almost two years of ageing at 65.5°C there is still significant levels of EC (Fig. 15 D). This fact was also observed by another author (143) who attributes this to NQ which seems to behave like a stabilizer. However, only experience will demonstrate if this behaviour is characteristic of every triple base.

4.6 Calibration Methods

As described in Sections 4.4 and 4.5, EC is used as an internal standard for the DPA method, while DPA is used for the EC method. The addition of an internal standard is a widely used technique for quantification using both peak heights and peak area. The internal standard compensates for various analytical errors. With this method of quantification, a known compound at a fixed concentration is added to the unknown sample to give a separate peak on the chromatogram. In order to illustrate how the DPA and EC HPLC methods work, they were applied to two powders for which DREV was requested to test the chemical stability.

The first example is a single-base powder manufactured in 1990 by Expro Chemical Product, so it is a relatively new powder. This powder is stocked in a DREV magazine and this test was required by the Armaments Division to fulfil security regulations. The sample was prepared according to the method described in the next Section and the chromatogram recorded is illustrated in Fig. 16 B. The first peak at about 5 min. is due to the DBP of the previous injection, as explained in Section 4.4, and identified on the chromatogram are peaks for DNT, 4-NDPA, N-NO-DPA, DPA, EC (the internal standard) and 2-NDPA. As expected, since it is a fairly new gun powder the degradation mechanism has not proceeded to great extent. The quantification of DPA and N-NO-DPA was done by the internal standard calibration method.

The internal standard used for the method for DPA-stabilized propellant is EC. First, a standard solution containing the products to be quantified and the internal standard is prepared and injected into the HPLC in order to calculate the response factor for each product to be quantified. For example, a standard solution containing 0.1280 mg/ml of EC, 0.2401 mg/ml of DPA and 0.2449 mg/ml of N-NO-DPA was

injected in the HPLC and the chromatogram in Fig. 16 A was recorded. The areas of the N-NO-DPA, DPA and EC peak were respectively 2879, 3291 and 2443 mA*s. The response factor for a compound *i* is given by :

$$K_{F_i} = \frac{m_i}{m_{IS}} \cdot \frac{A_{IS}}{A_i}$$

where m_i = mass of compound *i* in the standard solution,

m_{IS} = mass of the internal standard in the standard solution,

A_i = area of the compound *i* peak,

A_{IS} = area of the internal standard peak.

Thus according to the value given above:

$$K_{F_{DPA}} = \frac{0.2401}{0.1280} \cdot \frac{2443}{3291} = 1.3924$$

$$K_{F_{N.NO.DPA}} = \frac{0.2449}{0.1280} \cdot \frac{2443}{2879} = 1.6235$$

Hence, the amount of compound *i* in the powder is given by :

$$i\% = \frac{m_{IS}}{M_p} \cdot \frac{A_i}{A_{IS}} \cdot K_{F_i} \cdot 100$$

where m_{IS} = mass of internal standard added to the sample solution,

M_p = mass of the powder dissolved in the sample solution,

A_i = area of the ingredient *i* peak in the sample solution chromatogram,

A_{IS} = area of the internal standard peak in the sample solution chromatogram.

K_{Fi} = response factor for compound *i*.

For example, the chromatogram illustrated in Fig. 16B was produced by dissolving 1.0492 g of M1 powder in 48 ml of acetonitrile (ACN), 2 ml of an internal standard solution (349.6 mg of EC in 25 ml ACN) was added and finally 10 ml of a water solution containing 2% of CaCl_2 was added in order to precipitate the NC. An aliquot of the supernatant liquid was transferred into a vial and 5 μL was injected into the HPLC. Thus for this solution:

$$M_p = \frac{1049.2 \text{ mg}}{60 \text{ ml}} = 17.4867 \text{ mg/ml}$$

$$m_{IS} = \frac{349.6 \text{ mg}}{25 \text{ ml}} \times \frac{2 \text{ ml}}{60 \text{ ml}} = 0.4661 \text{ mg/ml}$$

In chromatogram illustrated in Fig. 16 B the areas for the N-NO-DPA, DPA and EC peaks are respectively 198, 3816 and 13115 mA*s. and consequently :

$$\%_{DPA} = \frac{0.4661}{17.4867} \times \frac{3816}{13115} \times 1.3924 \times 100 = 1.08\%$$

$$\%_{N-NO-DPA} = \frac{0.4661}{17.4867} \times \frac{198}{13115} \times 1.6235 \times 100 = 0.07\%$$

The second example is an M8 powder which was sent to DREV in 1993 after it had failed the Abel heat test. This powder was manufactured in 1990 and was therefore a relatively new powder, and consequently the Abel heat test result was questioned. The chromatogram for the standard solution is illustrated in Fig. 17 A. This standard solution contained 0.2040 g/ml of EC and 0.1910 mg/ml of DPA and the area of the EC and DPA peaks were respectively 3653 and 2421 mA*s. The response factor for EC is given by:

$$K_{F_{EC}} = \frac{0.2040}{0.1910} \times \frac{2421}{3653} = 0.7078$$

The sample solution was prepared by the dissolution of 1.0308 g of the powder in 49 ml of ACN and 1 ml of the internal standard solution (0.5626 g of DPA in 50 ml ACN). The NC was precipitated by the addition of 10 ml of a 2% CaCl₂ solution in water. The chromatogram of this solution is given in Fig. 17 B and the area of the DPA and EC peaks were respectively 2657 and 1475 mA*s. Thus, the percentage of EC in the M8 powder is:

$$\% EC = \frac{0.1883 \text{ mg/ml}}{17.1833 \text{ mg/ml}} \times \frac{1475}{2657} \times 0.7078 \times 100$$

$$\% EC = 0.43 \%$$

As we will see later, this level of EC means that the powder is stable for at least two years and this is an example of a false alarm given by the Abel heat test. A situation such as this has occurred several times in the past.

All these calculations can be done with software provided by the HPLC manufacturer and the details are given in the manufacturer reference books (144, 145). A calibration curve is built from at least three different standard solutions covering the concentration range of the compounds of interest. The response factors are calculated from the slope of these calibration curves. Afterwards, this software calculates the percentage of the compounds of interest from the area of the corresponding peaks in the chromatogram of the gunpowder solution. It is worth noting that peak area was used in the above examples, but peak height can be used as well. The choice between peak height or peak area measurements depends on several factors as discussed in

detail in Refs. 146 and 147. However, since the methods developed give rise to well resolved peaks that are free of interference, in our opinion, the peak area method can be used with confidence for the quantification of DPA, N-NO-DPA and EC.

The above-described internal standard calibration method works well if the internal standard is not an ingredient nor an impurity in the powder analyzed. Such a situation is not expected to occur, according to the list of powders given to us by the CF (see Tables I and II), since all the listed gunpowders are either DPA- or EC-stabilized. On the other hand, it is quite possible that during the processing of a gun powder an impurity such as DPA or EC could be present from a previous mix.

Fortunately, if a such situation occurs, it would be easily detected since the internal standard peak is always approximately the same height or area because the same known amount is added to the powder solutions. Consequently, any abnormal height or area for the internal standard peak will be an indication of the presence of the latter as an impurity in the unknown being analyzed. To illustrate such a situation, a DREV study on a ball powder will be used. However, for this study, a different HPLC method was used. This method is used at DREV for research purposes and it gives good resolution (> 1.5) for almost all DPA derivatives up to the trinitro-DPA. In this method the same column as the one for the DPA method (Section 4.4) is used, but a tertiary mobile phase is used (22% MeOH/36% ACN/42% water) with a flow rate of 0.7 ml/min.. This explain the longer retention times in Figs. 18 and 19 and the different elution order compared with the DPA method described in Section 4.4.

Figures 18 A, B and C are the chromatogram obtained for three standard solutions. Each solution contains 0.121 mg/ml of EC and the average area for the EC peak is 6,676,892 $\mu\text{V}\cdot\text{s}$. (the unit differs from the previous one since for this example

the DREV HPLC was used). On the other hand, Fig. 19 B is the chromatogram of a ball powder for which 0.121 mg/ml of EC was added and the area of the EC peak is 2,989,783 $\mu\text{V}\cdot\text{s}$., that is about 12 % higher than the corresponding area in the standard solutions. This clearly indicates that there is an impurity coeluting with the standard EC. In fact, this was confirmed by the chromatogram illustrated in Fig. 19 A of a solution of the ball powder for which no EC was added. As observed at about 31 min., there is a peak for which the UV spectrum and the retention time correspond to those of EC. This means that EC was present in this ball powder as an impurity and in such a situation either another internal standard or another calibration method must be used. However, the search of another internal standard is not an easy task. Therefore, the external calibration method will be used since all the figures needed for this method of calibration are already available from Fig. 18.

For the external standard calibration method, a calibration plot (conc. vs. area or height) is built from the chromatograms of at least three different concentrations of the sample of interest covering the range of concentrations expected in the sample solution. From the linear regression of this plot, the amount of the sample in the unknown solution is determined. For instance, the concentrations of DPA and N-NO-DPA used in Figs. 18 A, B and C and the corresponding areas are given in Table X. From these values, a calibration plot (conc. vs. area) is built and the value for the slope, the y-intercept and the correlation coefficient are also given in Table X. Next, 0.9963 g of the ball powder is dissolved in 60 cc of ACN (16.605 mg/ml). The chromatogram of this solution is illustrated in Fig. 19 B. The area for the DPA peak and the N-NO-DPA peak are respectively 5 656 873 and 1 572 387 $\mu\text{V}\cdot\text{s}$. and substitution of these values in the linear regressions given in Table X yield 0.1455 mg/ml for DPA, which corresponds to 0.88%, and 0.0449 mg/ml for N-NO-DPA, which corresponds to 0.27 %.

Which calibration method should be used? Actually, all the calculations can be done with software provided with the HPLC instrument (144, 145) and, in both cases, at least three standard solutions covering the range of concentrations expected in the powder must be done. The same solutions can be used for both calibration methods and therefore both can be used without any additional effort. However, the internal standard method is known to be more precise, especially when a sample workup is needed prior to the injection, which is the case for this analysis as it will be discussed in the next section. In fact, the internal standard can compensate for the loss of the compound of interest during sample workup. However, the internal standard must be structurally similar to the compounds of interest and, in this way, it is hoped that the loss of the compound of interest will be accompanied by the loss of an equivalent fraction of the internal standard. Besides being structurally similar the internal standard must have a retention time close to the compounds of interest and it must have a completely resolved peak free of interferences. Unfortunately, in this work several compounds structurally similar to DPA or EC were tried but none were found with an acceptable retention time, except EC for the DPA method and DPA for the EC method. However, as will be discussed in the next section, there is no coprecipitation of DPA, N-NO-DPA and EC during the sample workup and consequently the external standard method should be reliable. However, as discussed above both methods can be used simultaneously without any additional work and the use of both calibration methods is recommended.

4.7 Method for Sample Preparation

As described in Section 4.6 prior to HPLC analysis the gunpowder is dissolved in ACN, an internal standard is added and the NC is precipitated by the addition of 10 ml of water containing 2% of calcium chloride. This last step is needed in order to eliminate NC from the solution and thereby preventing the plugging of the HPLC

column by NC. Indeed, NC is soluble in ACN however, it is less soluble in a mixture of ACN and water and consequently, if water is not added to the solution the NC would be precipitated in the column by the mobile phase which consist of ACN-water mixture. With time, this NC precipitation would plug the column and significantly reduce its lifetime. Moreover, this NC precipitation will raise the operating pressure during the analysis with the consequence of a higher wear rate for the various instrument components. This is why NC is precipitated prior to injection into the HPLC. However, it can be argued that, during the precipitation of NC, the stabilizer may coprecipitate, as was observed when NC was precipitated with water from a methanol solution (19).

On the other hand, a study (117) showed that when the NC is precipitated with an aqueous CaCl_2 solution from an ACN solution of the powder, there is no coprecipitation of DPA or EC. The same conclusion was reached among participating countries of an ad hoc group that prepared upgrade of NATO STANAG 4117. Nevertheless, for the sake of completeness, we have also done some experiments to verify if there is coprecipitation of stabilizer during the NC precipitation.

The first experiments were done to verify if DPA coprecipitates with NC during the analysis of a relatively unaged single-base gunpowder (M1). The analysis was done three times and for the first three samples, the NC was not precipitated and for the last three the NC was precipitated by the addition of 10 ml of an 2% CaCl_2 aqueous solution. The concentrations of DPA were found to be 1.05 % ± 0.01 for the first three (no precipitation) and 1.08 % ± 0.03 for the last three (NC precipitated). These results show that the differences in concentration of DPA with and without NC precipitation are not statistically significant and consequently indicates no coprecipitation of DPA or its derivatives during the NC precipitation step.

As will be discussed in a later section, the sentencing criteria for DPA-stabilized propellants are based on the level of effective stabilizer which includes some daughter products of DPA. Therefore, the coprecipitation of the first daughter products of DPA must be studied. Hence, the same experiments as those described above were repeated with an aged single-base powder and the results obtained are given in Table XI. As can be observed, the differences are not statistically significant for the mono-nitro, di-nitro and mono-nitro N-nitroso derivatives of DPA. This demonstrates that, during the NC precipitation step, there is no coprecipitation of DPA or its first daughter products.

In order to check if EC is precipitated during the NC precipitation, the same type of experiment was done on a slightly aged double-base propellant (M8), an aged double-base propellant (AKB 204), a slightly aged triple-base and, finally, on an aged triple-base. The results are given in Table XII and a simple visual inspection shows that the differences are not statistically significant and again this demonstrates that the NC precipitation step does not have any influence on the EC concentration. Since the sentencing criteria for EC-stabilized propellants are based on the EC concentration only, no attention was paid to study the coprecipitation of EC daughter products in this work.

The solvent used for the sample preparation is ACN. It is well known that ACN is expensive and its disposal is difficult. Nevertheless, as described above when this solvent is used there is no problem of coprecipitation and this is the standard method used by NATO countries (STANAG 4117). Furthermore, the use of ACN with the addition of water results in an injection solvent very close to the mobile phase used in the two methods. This procedure is strongly recommended in HPLC since it avoids many pitfalls. However, for cost-effectiveness, the laboratory responsible for the testing might prefer to use another solvent.

In this situation, the laboratory must test its new solvent against the standard method to make sure that there is no problem of coprecipitation. However, in this work a standard procedure was established to simplify future work. Indeed, there is no need to test a new solvent for non precipitation of NC, a harsh procedure for the column. Instead, the new solvent procedure must be compared with the ACN procedure, a standard procedure which has been tested worldwide and has shown no problem of coprecipitation.

Regarding possible solvents that can be used to replace ACN, the following recommendations should be helpful: A solvent such as methylene chloride should be avoided since it has been shown (107) that its injection in amounts greater than 2 μ l tends to interfere with reverse phase separation. A plausible candidate could be acetone since this solvent is used in France. However, it is important to stress that any change of solvent for the preparation of the sample must be tested against the standard method described in this section and furthermore additional tests must be done to make sure that the new solvent does not interfere or impair the HPLC methods developed in this work.

4.8 Reproducibility and Reliability of the Methods

In this section, we will discuss the tests that were performed to verify the two methods developed in terms of reproducibility and reliability. First, several injections of the same solution were done to determine the reproducibility. Secondly, the pitfalls that can be encountered during the HPLC analysis of basic compounds will be discussed as well as the procedure that should be followed to avoid the problems caused by these types of compounds. Thirdly, the stability of the results as a function of time will be checked. Finally, the results obtained with the DPA method will be compared with those obtained in another country on the same gun propellant.

In order to evaluate the reproducibility of the two methods, a solution of a DPA-stabilized propellant and a solution of an EC-stabilized propellant were prepared according to the method described in Section 4.6. These two solutions were analyzed with their respective HPLC methods. In each case, 72 injections were performed as well as a calibration at the beginning and periodical calibrations after every twelve injections. The results obtained are given in Tables XIII and XIV. It is obvious from these two tables that the two methods are highly reproducible. On the other hand, it should be noted that in Table XIII, the KF_i for DPA is slightly more variable than the N-NO-DPA KF_i . This could be explained by undesirable interactions between the DPA and residual silanol groups on the silicate substrate of the column. In fact, it has been shown that more or less irreversible absorption of the DPA occurs on some columns (148). An example is illustrated in Fig. 20 for hypersil column, it is clear that at each injection some DPA is absorbed on the column. Certain packings are better for the analysis of basic compounds such as DPA (149, 150). The column used for this work does not show absorption of DPA and its first daughter products as illustrated in Fig. 21. However, according to Ref. 148 a column which is initially acceptable might develop DPA absorption with time. Although we did not experience any absorption problems during the course of this work, we strongly recommend that the analyses be performed according to the procedure used in Tables XIII and XIV. That is with periodic calibrations in order to monitor the DPA KF_i and the occurrence of any erratic behaviour. In addition to this, in the event of minor DPA absorption, the periodic calibrations, will upgrade the DPA KF_i value at regular intervals and in this way minimize the error in the calculated value for the DPA concentration.

It is well known that problems with basic compounds in reverse phase HPLC can be solved by the addition of a silanol masking agent such as triethylamine (TEA). However, in this work the addition of TEA to our mobile phase caused a rather noisy baseline and the same observation was made in Ref. 148. Furthermore, some

disadvantages are also inherent when amine additives are used. First, they add to the cost and preparation time of the mobile phase (151). They can also change column selectivity and make the use of the column for other applications difficult. However, it must be stressed that during the course of this work we have not experienced any problems due to DPA absorption onto the column. We do observe that the DPA KF's were slightly more variable than those of other derivatives but, this small effect is easily accounted for by periodic calibration and consequently it was decided to not use an amine additive.

It might be interesting to check the consistency of the results obtained by the two methods over a long period of time. This was done by doing the analyses of the same propellants at different time intervals. The results are given in Table XV and as indicated, the two methods appear to be stable and reliable over time. This is particularly interesting since the analyses were done with columns from different batches.

Finally, in the course of a project under the Franco-Canadian Accord, we had the opportunity to compare the results obtained with our DPA method with the results obtained by the French. Unfortunately, double- and triple-base propellants were not included in this exchange and therefore the EC methods were not compared. In this exchange, the French sent three gun propellants to Canada. The first one (powder 1) was manufactured recently, the second one (powder 2) was about 10 years old and the third one (powder 3) was over 30 years old. The amount of DPA and N-NO-DPA for these three powders were determined by each country using its own HPLC method. The results are given in Table XVI. As indicated, the agreement between the two countries is excellent for powders 1 and 3, however, there is a discrepancy between the two countries for powder 2. This discrepancy can be explained by the heterogeneity of the sample. In fact, Table XVII gives the results obtained by each

country from the analyses of three individual grains of powder 2. It is clear from these results that there is a strong variation in the concentrations of DPA and N-NO-DPA from grain-to-grain and these variations could explain the discrepancy observed. Therefore, the heterogeneity into the sample explains the discrepancy and consequently there is an excellent agreement between France and Canada which is an additional proof of the reliability of our DPA method. However, the occurrence of such high variability in the stabilizer concentration from grain-to-grain of the same lot of gun powder can have serious consequences from the security point of view and this fact must be taken into account for the sampling of the gun propellant prior to the HPLC analysis as will be discussed in more details in Section 5.5.

4.9 Column Performance Monitoring

The equation below shows the factors affecting separation.

$$R_s = 0.25N^{0.5}(\alpha-1) [k/(1+k)]$$

where N is the column plate number, k is the retention factor and α is the ratio of k values for adjacent peaks. The α and k values are related to the mobile phase composition which has already been optimized during the development of the methods. However, the mobile phase composition requires slight adjustments to compensate for column-to-column variation and the procedure used for a new column was described in Section 4.4. However, the column plate number (N) starts at an optimum value for a new column and decreases as the column ages. This is caused by deterioration of the column packing due to chemical reactions in the chemically bonded organic stationary phase, absorption of strongly retained impurities, etc. Therefore, this deterioration of the column affects its N value and a point could be reached where the resolution is inadequate and as a result, the precision of the methods can be impaired.

Consequently, a procedure must be included to ensure the quality of the column and to avoid the pitfalls that can impair the reproducibility, the reliability and the precision of the HPLC methods. The following is a description of such a procedure.

At the beginning of the column life, the first step is the optimization of the mobile phase composition (α and R) as described in Section 4.4 to obtain maximum resolution and this is done with the DPA method for which the resolution of the critical pairs 2,4'-DNDPA/N-NO-DPA is the most critical. The second step is the determination of the column plate number (N) which can be evaluated according to the following equation:

$$N = 5.54 \left(\frac{t_r}{W_r} \right)^2$$

where: t_r is the solute retention time

W_r is the bandwidth of the solute peak at half height.

Although this can be calculated by hand, it is prone to high experimental error, and therefore it is strongly recommended that a computer-based evaluation of N be used to ensure the accuracy of the results. As discussed in Section 4.4, the degradation of the column will also affect the k value initially set during the solvent optimization step. The k value for a given solute is given by:

$$k = \frac{t_r - t_0}{t_0}$$

where: t_r is the solute retention time

t_0 is the retention time for an unretained solute

These two parameters N and k should be monitored on a periodic basis. For example, each morning a standard solution containing DPA, N-NO-DPA and EC should be injected, separated by the DPA method and the three values of N and the three values of k are recorded and the evolution of these values are used to sentence the column. For instance, a diminution of more than 25% of N and/or a variation of more than 3% of k indicate the end of the useful life of the column.

Finally, a guard column can be used to prolong the useful life of a column. Throughout this work, short guard columns from the same suppliers as the analytical column (E. Merck), filled with the same stationary phase, were used. These guard columns are replaced at specific intervals. They cost a fraction of the price of the more expensive analytical column and they protect the latter against strongly retained sample components.

5.0 APPLICATION TO A SURVEILLANCE PROGRAMME

5.1 Introduction

As discussed in Section 2.1, the thermal degradation of nitrate esters produces heat and as a result the temperature of the powder rises. If the heat generation exceeds the heat loss to the surroundings, self-ignition might occur. Stabilizers such as DPA and EC are added to gunpowder formulations to delay the nitrate ester degradation. During this process, the stabilizer is consumed and the more the stabilizer is depleted the higher are the risks of self-ignition. Therefore, the level of residual effective stabilizer (RES) of a gunpowder must be monitored at regular time intervals in order to detect those powders with uncertain chemical lifetimes. The two HPLC methods developed in this work are the tools that will be used to determine the RES.

Indeed, these tools can be used both for a surveillance programme as well as an acceptance procedure such as NATO STANAG 4117. STANAG 4117 is a procedure that guarantees to a buyer that the chemical lifetime of the purchased powder will be 5 or 10 years. In other words, this is a procedure that guarantees that a new powder will age properly and that there is nothing in the powder that can impair its chemical stability. However, since gunpowders age very slowly at normal storage temperatures, an artificial accelerated ageing is needed. For instance, STANAG 4117 included a period of heating at 65.5 °C for 60 days to obtain a 5-year guarantee or 120 days for a 10-year guarantee. After the heating period, the RES is determined and the powder sentenced according to the difference in RES before and after the accelerated ageing. The last version of STANAG 4117 allows the use of HPLC to determine the RES.

It is possible to use an acceptance procedure such as STANAG 4117 in a surveillance programme. For instance, each 5 years the powder should be submitted to a 60 days heating period to guarantee another 5-year period. Of course, such a procedure is cumbersome and expensive; moreover, if the powder fails the 5-year criterion it is impossible, with this procedure, to determine the remaining safe lifetime for the powder. Furthermore, as discussed in Section 2.3, the ageing process is dependent on several variables such as the storage temperature, temperature cycle, humidity conditions etc. As 5-year period could be too long in some instances, a more discriminating procedure would be required.

5.2 The Surveillance Programme

The following procedure is recommended to monitor the chemical stability of all gunpowders purchased, used and stocked by the Canadian Forces.

First, each time a new lot of gunpowder is purchased, a 5-year STANAG 4117 (if applicable) must be required from the seller or done by the CF. This will guarantee that the lot purchased ages properly. It might be argued that a such procedure is cumbersome but this is needed only when the powder is purchased and this test is often performed by the distributor. This test is worthwhile if one take into account the problems encountered as a result of the risk of self-ignition and the associated expenses whith a lot with doubtful stability is bought.

Secondly, after this 5-year period, the chemical stability of the powder must be monitored by the determination of the RES with the HPLC methods developed in this work. Once the level of RES of a given gunpowder has been determined, this figure is used to determine its useful safe lifetime according to the sentencing criteria given in Table XVIII. A first version of a standard operating procedure (SOP) for the determination of the residual effective stabilizer for DPA- or EC-stabilized gun powders has been written and will be published later. This SOP was written from the works done in this paper and of course would need to be adapted over the years to the needs and particularities of the gunpowders purchased, used and stocked by the CF.

Finally, it must be stressed, that the HPLC methods developed in this work and the STANAG 4117 are only applicable for single-base propellant stabilized with DPA and double- or triple-base propellants stabilized with EC, which is the case for almost all the gunpowders used or stocked by the CF at the present time. Gun powders stabilized with other type of stabilizer or rocket motors are not adressed in this work but there is presently some research being done at DREV and in other NATO countries with respect to these applications.

5.3 Sentencing Criteria

In this section, the rationale behind the construction of Table XVIII will be discussed.

Countries such as France, the UK, the U.S. and Australia have developed their own sentencing criteria from observations and data collected over several years of gun powder chemical life testing. Therefore, they have acquired the data base, expertise, experience and history that allow them to set up appropriate sentencing criteria. On the other hand, to the best of the author's knowledge, no such expertise and data base have been acquired in Canada. Therefore, the only way to set up our sentencing criteria is to study those from other countries in order to determine if there is a general trend and from this, set up sentencing criteria to start with and adapt them according to the data base, experience and history that will be acquired over years of ageing of the gunpowder used by the CF.

Comparison of the different sentencing criteria from the UK (126), France (125), for the U.S. Navy (152) and in Australia (5), show that they are generally quite similar. In fact, the differences appear in the definition of the residual effective stabilizer (RES) and when the concentration of the residual effective stabilizer is low. However, it is still possible to set-up sentencing criteria using those of the four aforementioned countries.

One difference between the countries is the definition of the residual effective stabilizer for DPA stabilized gunpowder. In France, the RES is the summation between the DPA concentration and the molecular weight corrected concentration (MWCC) of N-NO-DPA, 2-NO₂-DPA and 4-NO₂-DPA while in the UK it is the sum between the concentration of DPA and the MWCC of N-NO-DPA. For the US Navy

the RES is the summation of the DPA concentration and the MWCC of N-NO-DPA and the mononitro and dinitro-DPA derivatives and at the other extreme is the Australian criteria (5) for which the RES is solely the DPA concentration. The molecular weight corrected concentration is the concentration of the derivative multiplied by the ratio of the DPA molecular weight (MW) to the derivative molecular weight. For example the MW of DPA is 168.23 while the MW of N-NO-DPA is 198.23 therefore, the MWCC of N-NO-DPA is the concentration of N-NO-DPA multiplied by 0.85.

Among these four countries the Australian criteria are the most severe since only DPA is considered an effective stabilizer. In fact, in Australia N-NO-DPA is not considered an effective stabilizer (16, 23). On the other hand, several studies (153-156) showed that N-NO-DPA was an effective stabilizer. Actually, except for the Australian and a laboratory in US, N-NO-DPA is considered throughout the world as an effective stabilizer and this is also our opinion as stated in a DREV study (157-158) which rejects the objections on which the Australian base their arguments against the role of N-NO-DPA as a stabilizer. Therefore, in Canada the effective stabilizer will be the sum of the DPA concentration and the MWCC of N-NO-DPA. It is with this RES definition that Table XVIII was constructed. Actually, the RES definition and the table were chosen in order to be in a middle position in comparison to the sentencing criteria of the aforementioned countries.

In fact, our sentencing criteria are less severe than the Australian since N-NO-DPA is included in our RES definition, while in Australia only the concentration of DPA is considered, but as discussed above, the Australian criteria are in our opinion too conservative. On the other hand, our sentencing criteria are more severe than the French because only DPA and N-NO-DPA are included in the RES, while in France, besides DPA and N-NO-DPA, the mononitro-DPA are also included in the RES.

However, it was our intention to be more severe than the French to compensate for the fact that microcalorimetry is used in France to confirm the stability of a gunpowder when the RES is smaller than 0.4 %. For instance, in France when the RES is smaller than 0.4% the powder should be retested in 1 or 2 years according to the heat flux measured in microcalorimetry. Now, if we look to our sentencing criteria in Table XVIII, such a situation corresponds to 20-40 % of RES since most DPA-stabilized gunpowder contains about 1% of DPA. As given in the table, the powder would then need to be tested in one year. The more severe alternative has been chosen in Canada since microcalorimetry will not be available as discussed in Subsection 3.1.4. Furthermore, since the French RES included mononitro DPA derivatives, it means that our sentencing criteria are even more severe. We recognize that this approach could be too severe but we believe that the potential risk associated with an unsafe gunpowder warrants this approach and, as discussed above, these sentencing criteria are simply a starting point and they will need to be adjusted as the CF acquire more data, experience and history on their stocked gunpowders.

Regarding the EC-stabilized gunpowders, all the aforementioned countries use only the concentration of EC as the RES. However, the sentencing criteria used in France, the UK and by the US Navy are similar or in line with those given in Table XVIII for DPA-stabilized gunpowders. Therefore, it appears that the same sentencing criteria can be applied to both types of powders. However, again there are some differences. For instance, the Australian criteria are more severe when the original EC level of the powder is greater than 3 %. In this case the maximum allowed loss of EC allowed is 2 %. For example, for a powder stabilized with 7.3% of EC, the powder is sentenced to be destroyed when the level of EC is lower than 5.3 % which is much more severe than the criteria given in Table XVIII. However, it must be stressed that gunpowders stabilized with an EC level greater than 3% are mainly double and triple bases which are reputed to age slowly and to be stable. Again, as discussed above,

these sentencing criteria are simply a starting point and it is only with the history acquired over the years that it will be possible to determine if these criteria are either too severe or adequate for our gunpowders.

Nevertheless, we are confident that the criteria of Table XVIII are strict enough to detect any powder with questionable chemical stability. Indeed, when the RES is less than 40 % the powder is considered to be uncertain and such a powder should be tested more frequently. Moreover, the use of such a powder should be considered a priority and must not be stocked or moved outside of Canada especially to a hot country.

Before closing this subject, it is important to note that to the best of the author's knowledge there is no study concerning the stabilizer role of EC daughter products in the literature. This could explain why only the concentration of EC is used in the sentencing criteria. This could also be due to the fact that the double- and triple-base gunpowders are presumed to be more stable than their single-base counterparts. Nevertheless, this presents an area of research that must be explored in the future as the need arises.

5.4 Small Calibers Gunpowders

With respect to the self-ignition hazard, it can be stated that the temperature of a propellant rises if its heat generation exceeds the heat loss to the surroundings. If an equilibrium can be established between the heat generation and the heat loss to the surroundings no self-ignition will take place. The heat loss to the surroundings is dependent on the storage temperature, the heat conductivity and the dimensions of the propellant mass in storage. Consequently, in munitions, the self heating of the powder mass increases with increasing diameter (or calibre) of the powder container. The

question now is: Is there a critical diameter under which there is no risk of self-ignition?

Several studies have been undertaken to answer this question (64-67, 159). It must be stressed that several hypotheses and simplifications are involved in these studies and it appears that the evaluation of the critical diameter is dependent on many parameters. Therefore, caution should be used before drawing any conclusions. Nevertheless, a French study (67) has shown that for a 30-mm calibre, very high heat generation is required to produce self-ignition at 50 °C. Therefore, it can be stated that under normal storage conditions, the risk of autoignition of a 30 mm or less munition is small. However, this statement is only valid under normal storage conditions, in other words, temperatures lower than 30 °C and low humidity levels. In fact, studies (64, 65) have shown that even a 30-mm munition may autoignite when violently subjected to a thermal stress, but self-ignition occurs from 70 °C which is not a normal storage temperature. Nevertheless, for economic reasons, it may be decided to not test 30 mm or less munitions and the CF must consider if it worth the cost and effort to test such munitions with low risk of self-ignition. For instance, munitions with low levels of stabilizer indicate NC degradation and risk of cartridge rust which could impair the ballistic properties of the munitions and consequently it might be worthwhile testing these munitions to detect these problems.

Nevertheless, in the event that the CF decides to test 30 mm or less munitions, the methods developed for the larger calibres in Tables V and VIII are applicable to most gunpowders used in small calibers. In fact, small caliber gunpowders used by the CF can be classified into three types:

1-) Double base stabilized with EC

ex: Bulleye

2-) Ball powders which are double base stabilized with DPA

ex: GBSE 105

SS 109 (contains DBP and DNT)

Unique 20

WC series (contain DBP)

3-) Single-base stabilized with DPA

ex: IMR 4895

IMR 5010 (contains DNT)

SPDN 1377 C (contains methyl centralite)

CMR 180

CMR 200

As can be seen from these formulations, the first type could be tested with the EC method and the last two types can be tested with the DPA method since no new ingredients other than those selected before are included in these formulations. It should be noted that the ball powders are double-base stabilized with DPA and are not addressed by STANAG 4117. However, the NATO countries are in the process of producing a new STANAG that will consider this type of gunpowder and it should be available in the near future.

5.5 Sampling of the Gunpowders

The aim of this work was to develop the necessary tools to monitor the chemical stability of gunpowders using modern techniques. However, one important aspect of a gunpowder surveillance programme has not been addressed in this work: the sampling of the gunpowders prior to HPLC analysis. Indeed, obtaining a sample representative of the total population is very important. It is imperative that the

sample of gunpowder withdrawn from a munition or a container be a sound representation of the whole lot of munition or the whole container.

Now that the tools to determine quantitatively the RES are available, the statistical aspect of the sampling must be studied as soon as possible. This is particularly important since, as discussed in Section 4.8 (Tables XVI and XVII), it is possible to have wide variation in RES level from grain to grain in the same lot of gunpowder. There are various causes which can explain such variations between two grains of the same gunpowder.

According to the French experience with DPA-stabilized gunpowder, it is common to encounter such high variation in the RES from grain to grain when the powder is in a rapid degradation phase. On the other hand, this could also be due to error during the gunpowder processing. For example, a certain quantity of stabilizer was added to half of the lot while a smaller quantity was added to the other half. Finally it can be simply due to an error during the analysis. Nevertheless, it is very important to distinguish each case. Indeed, the two first instances can have dramatic repercussions from the safety point of view compared to the third case. The only way this can be achieved is by making sure that both the sampling and the reliability of the laboratory are adequate. There is also a statistical treatment needed for the analysis of the results. It is recommended the analysis be done at least in triplicate and the following observation can also be of help: in general, the higher the powder is degraded, the higher is the standard deviation.

The sampling method will be dependent on several factors such as how the powder is stored (in bulk or in the munition), the location of magazine, the feasibility of opening several expensive amunitions etc. Nevertheless, for information only, we will describe how the sampling is done in a typical NATO country.

Ten munitions are randomly selected, opened and a 100 g sample is taken from each munition. A sample of 20 g of each of these 10 X 100 g is ground and the 10 X 20 g samples are mixed until homogeneous. This 200 g mixture is used for the HPLC measurement.

6.0 CONCLUSIONS AND RECOMMENDATIONS

In this work two fast, reliable and efficient high pressure liquid chromatography methods have been developed to determine the residual effective stabilizer of diphenylamine or ethycentralite gunpowders. These two methods will be used for the acceptance and the surveillance of the chemical stability of the gunpowders purchased, used and stocked by the Canadian Forces. Consequently the CF will be in a position to collect data and construct useful databases. In this way, it will be possible to develop an expertise and a history of gunpowders ageing and therefore to make sound predictions for the life expectancy of the munition.

However, there remains further research to be done. In our opinion, the most urgent one is to establish a sampling method that will produce samples representative of the total population. As a first effort, the analysis of all the gunpowders for two subsequent years could be performed with the sampling method that was used in the CF for the former Able heat test. In fact, the analysis of the results will give interesting insight regarding the dispersion, the pertinence of the sampling method and the identification of the doubtful lots.

Secondly, as discussed in Chapter 5, the sentencing criteria will have to be adapted to the gunpowders used and stocked in Canada. In regard to this topic, the microcalorimetry technique, discussed in Subsection 3.1.4, should prove to be very useful. This is the technique of choice to extend the lifetime of energetic compositions

and to make sound predictions about the remaining life. This technique can also prove to be essential for studies on predictive technology, a growing subject for the near future taking into account the budget cuts experienced by the Department of National Defence these days.

Thirdly, as discussed in Section 3.3, HPLC was preferred to gas chromatography because the latter can only be applied to relatively unaged DPA-stabilized gunpowders. However, after the first years of testing, the CF will have a better idea of the infrastructure needed, the real costs and the various changes and implications involved in this new surveillance programme. Moreover, the results might indicate that most gunpowders are stable and have a level of residual stabilizer higher than 60 % of the original one. Taking into account all the aforementioned parameters it might be cost-effective for the CF to consider the use of gas chromatography to screen the propellant and then to send only the powders which had failed the GC to a central laboratory. Of course, DREV could develop a GC procedure for this purpose.

Finally, DREV was tasked to develop modern methods for the determination of stabilizers in gunpowders. However, these methods can be applied, with reserve, to other energetic compositions stabilized with DPA or EC such as rocket motors and explosives. However, these other energetic formulations have not been considered in this work nor have the formulations stabilized with other stabilizers such as askardite been considered. Nevertheless, if in the future the CF would like to extend these methods to formulations other than those considered in this task, it would be possible for DREV to perform the work in a relatively short time frame. In the meantime, DREV will continue research work on this topic and this expertise is of course available for the future needs of the Canadian Forces.

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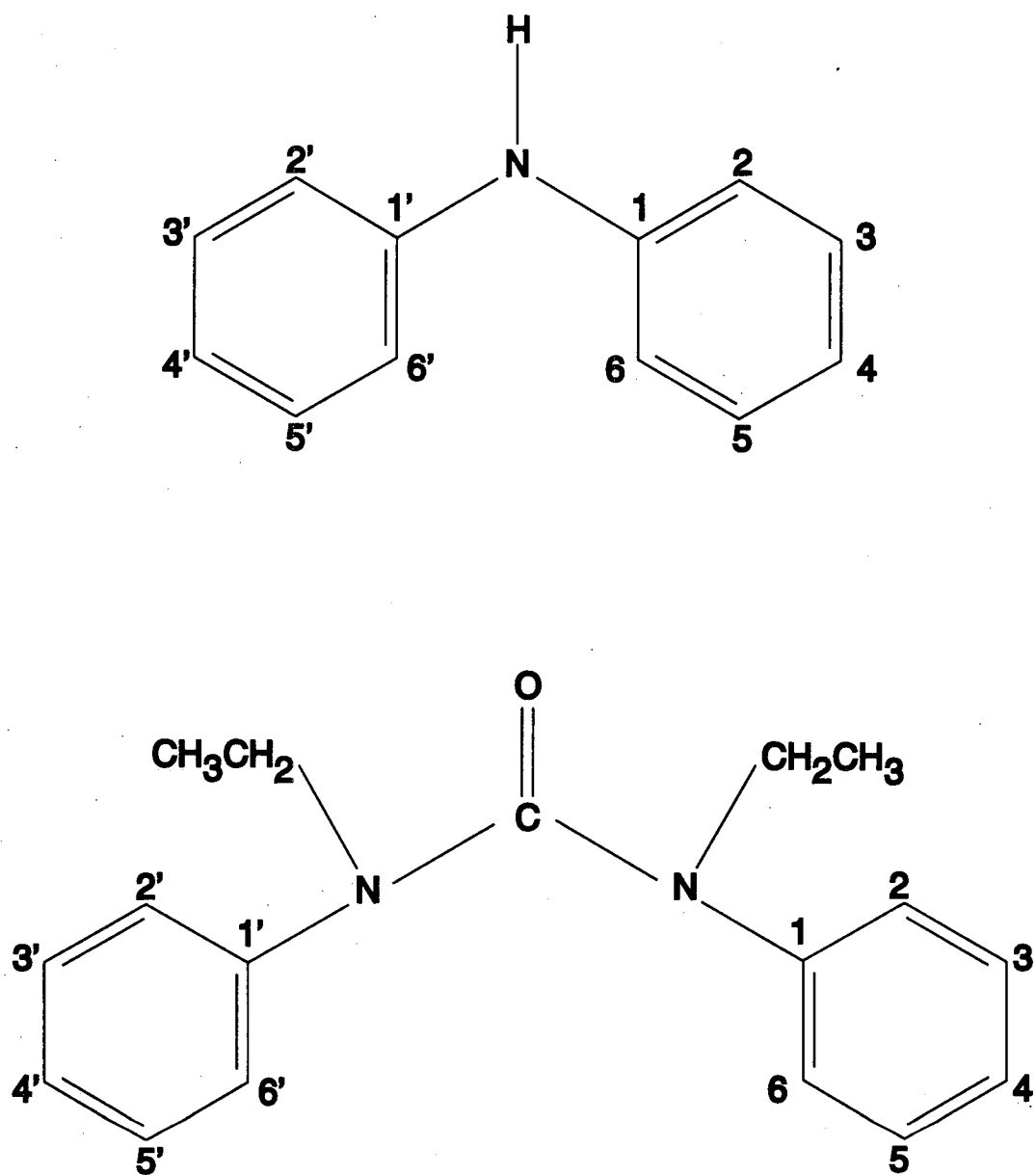
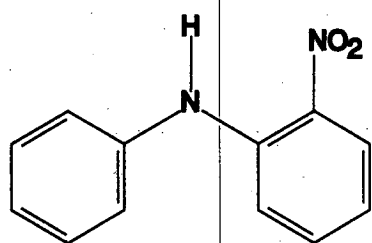
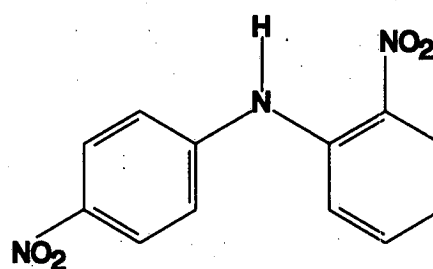
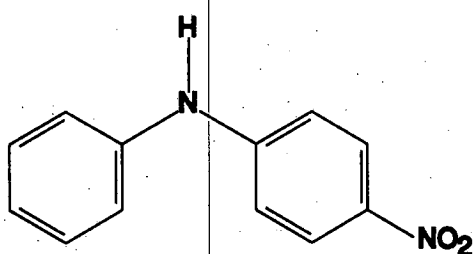
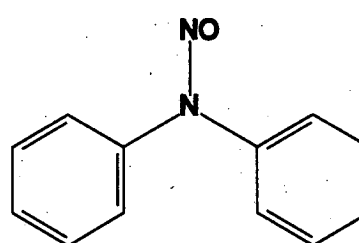
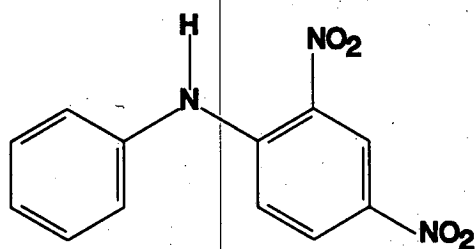
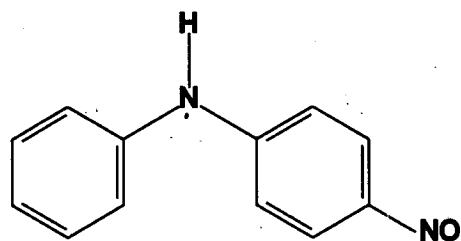


FIGURE 1 - Chemical formula of DPA and EC:
A-) Numbering system for DPA;
B-) Numbering system for EC.

A-) 2-NO₂-DPAD-) 2,4'-DI-NO₂-DPAB-) 4-NO₂-DPA

E-) N-NO-DPA

C-) 2,4-DI-NO₂-DPA

F-) 4-NO-DPA

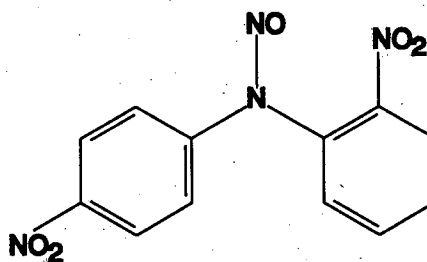
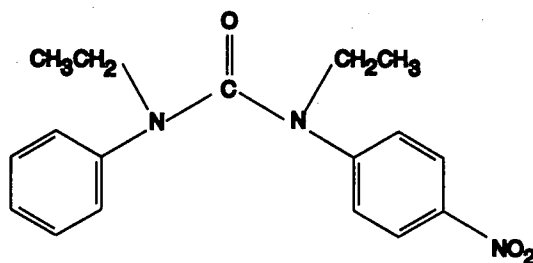
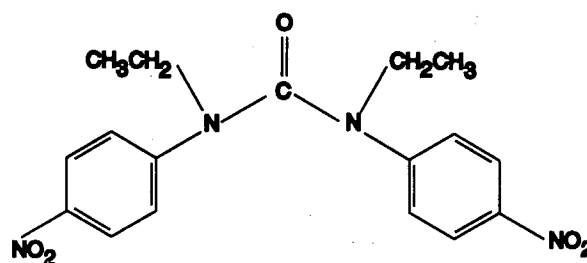
G-) N-NO-2,4'-DI-NO₂-DPA

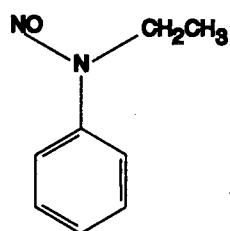
FIGURE 2 - Chemical structure of some DPA derivatives



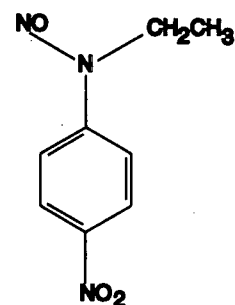
A-) 4-NO₂-EC



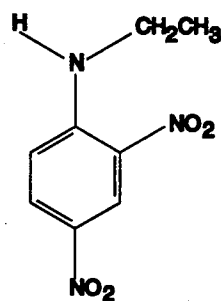
B-) 4,4'-DI-NO₂-EC



C-) N-NO-N-ETHYLANILINE



D-) N-NO-4-NO₂-N-ETHYLANILINE



E-) 2,4-DI-NO₂-N-ETHYLANILINE

FIGURE 3 - Chemical structure of some EC derivatives

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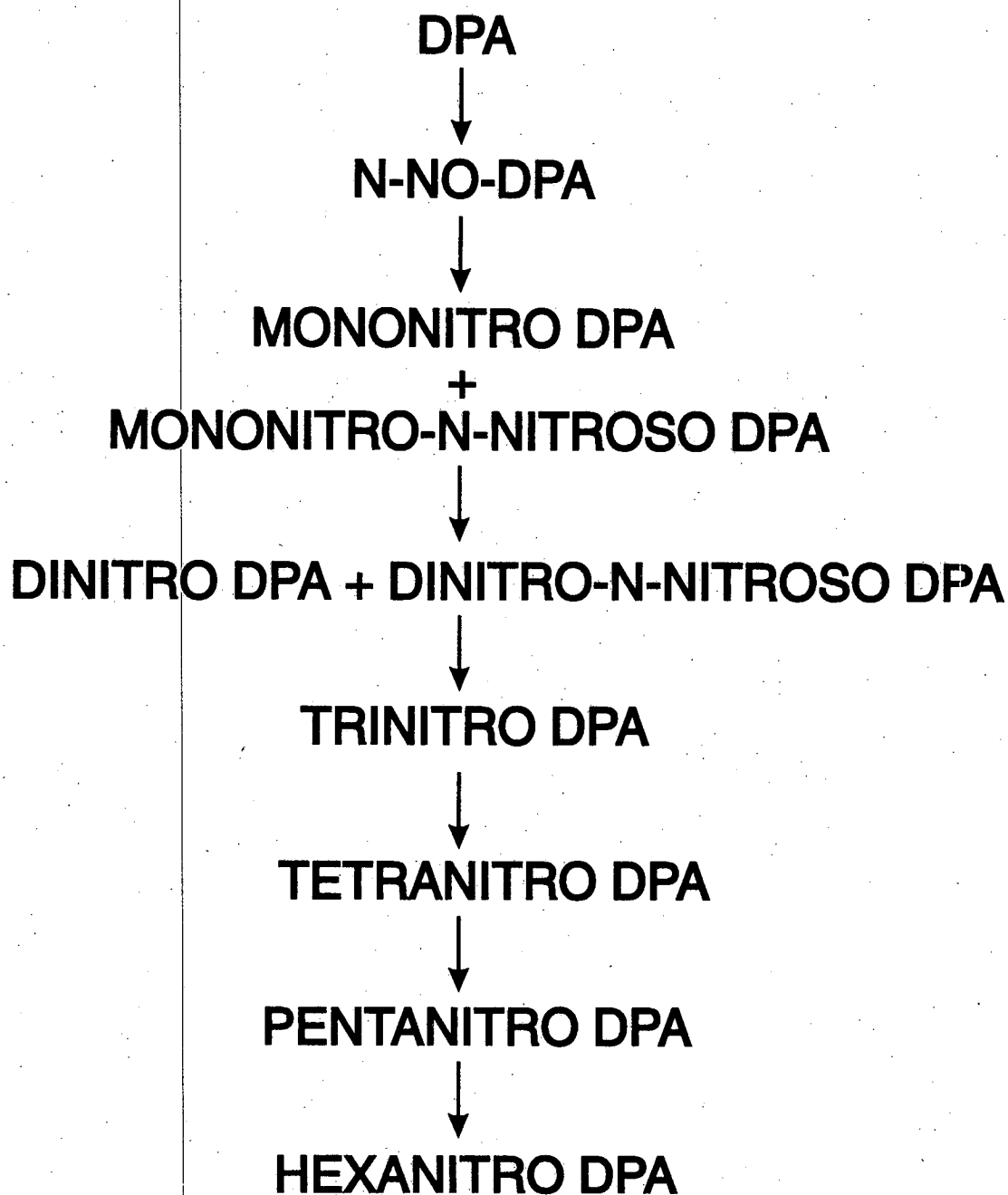


FIGURE 4- Reaction scheme for DPA

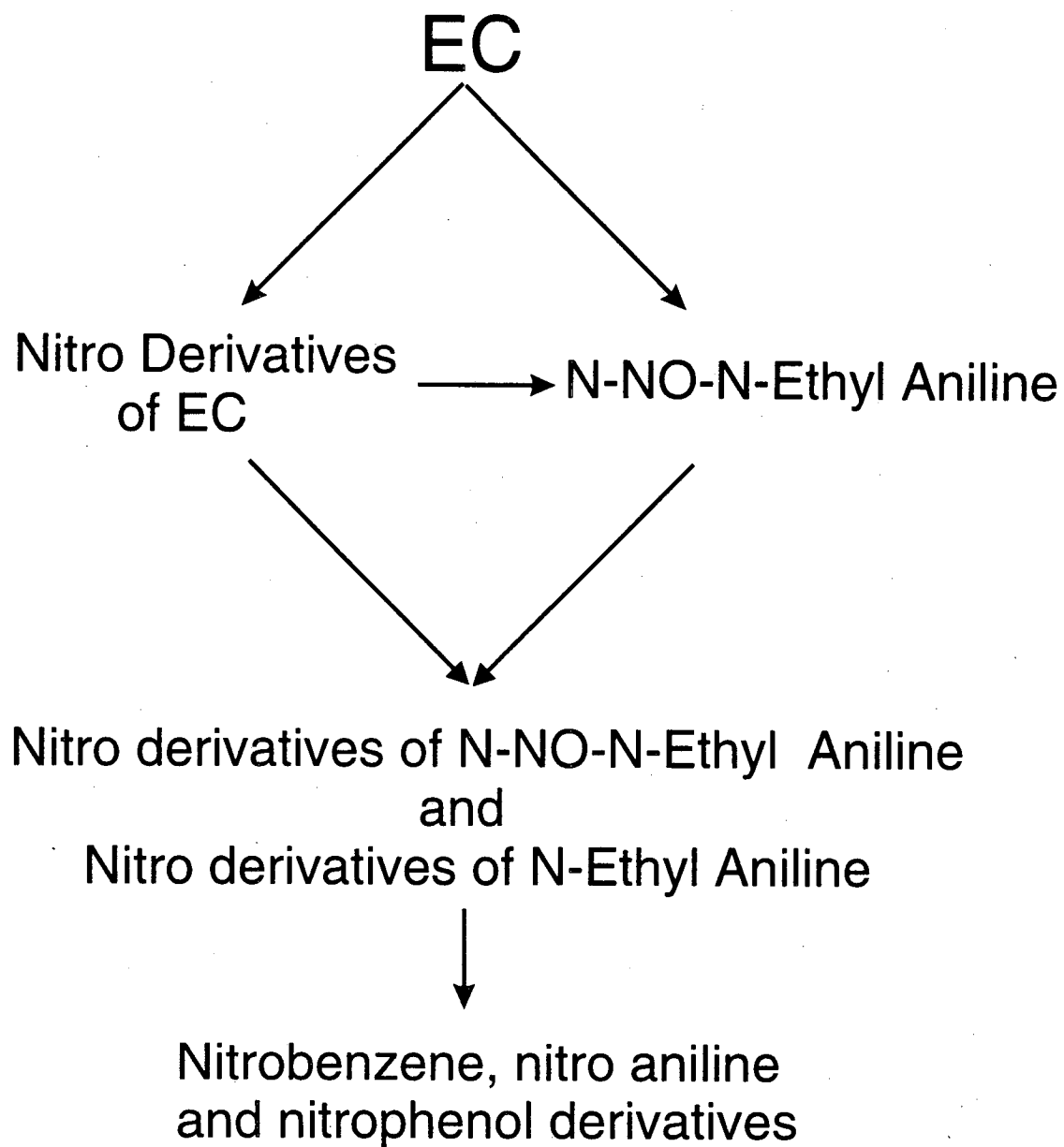


FIGURE 5- Reaction scheme for EC

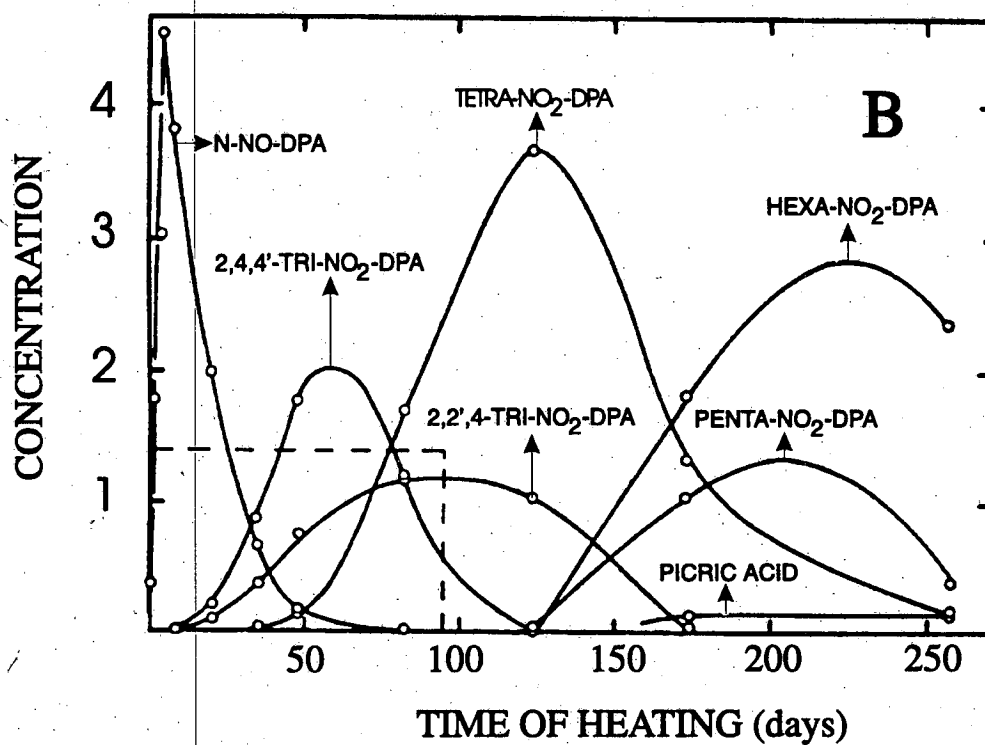
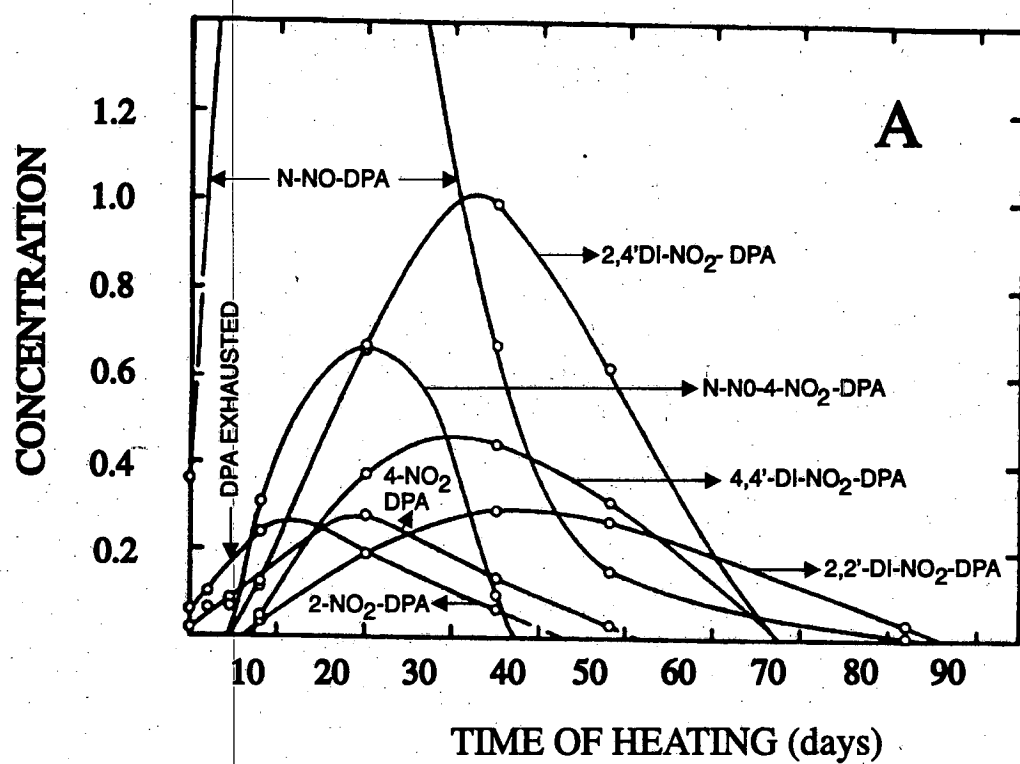


FIGURE 6- Concentration versus time of ageing plot for:
 A-) DPA and its first derivatives;
 B-) DPA higher nitrated derivatives.

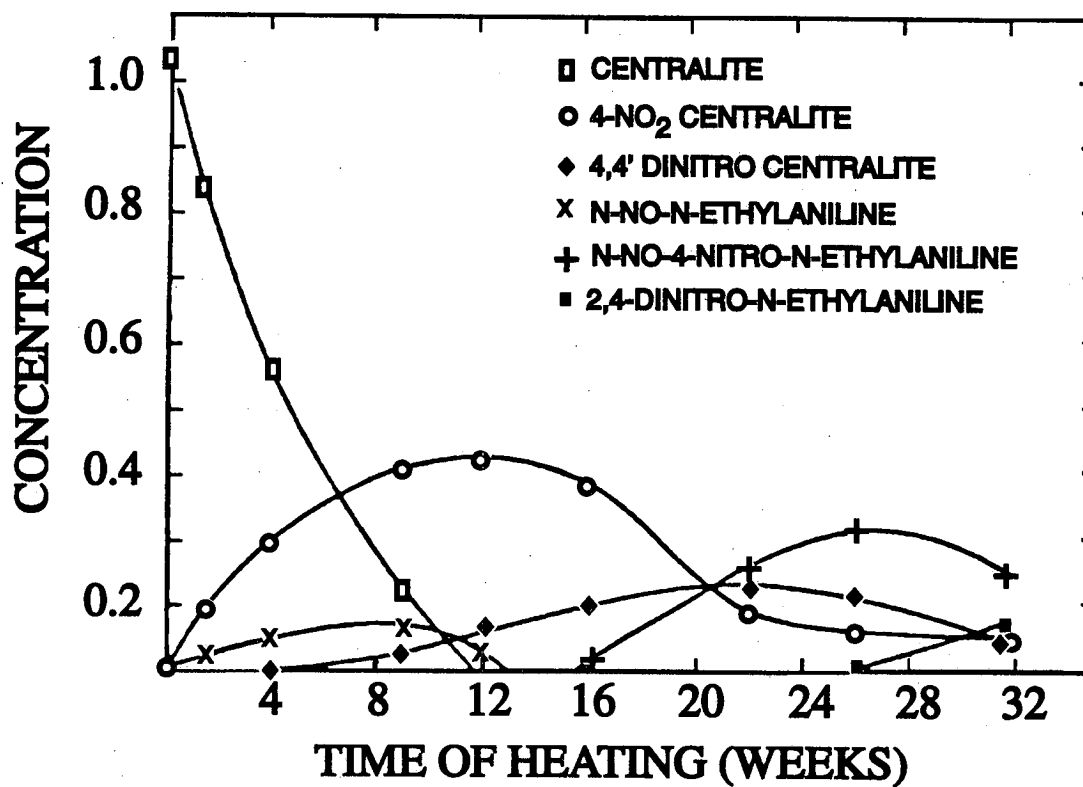


FIGURE 7- Concentration versus time of heating plot for EC and some of its derivatives

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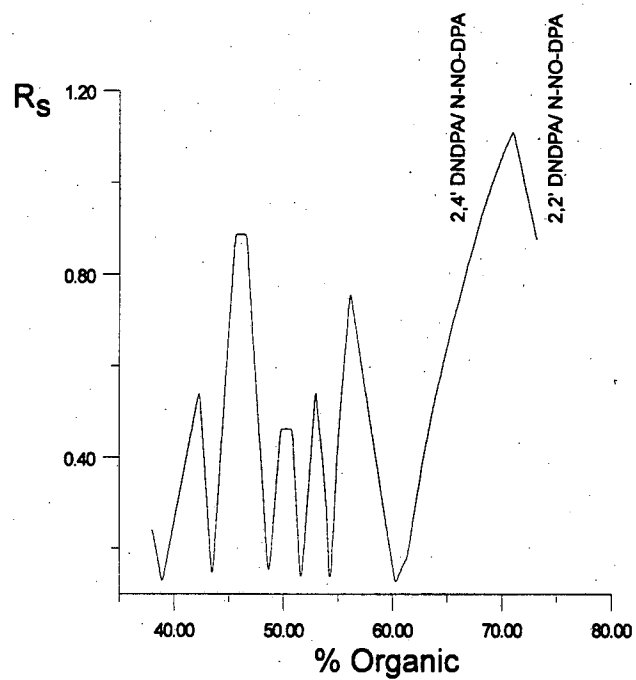


FIGURE 8 - Resolution map for N-NO-DPA

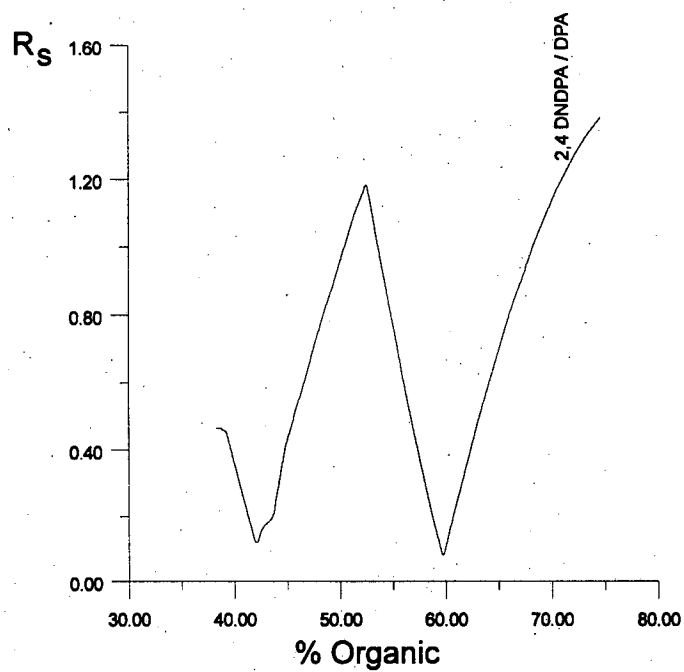


FIGURE 9 - Resolution map for DPA

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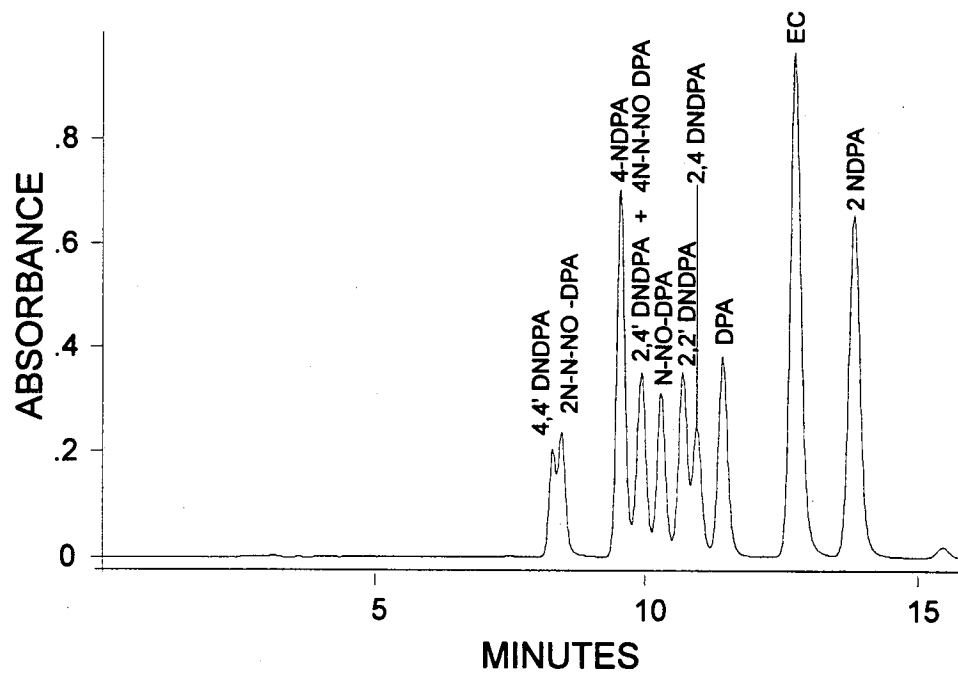


FIGURE 10 - Chromatogram for the first ten DPA derivatives

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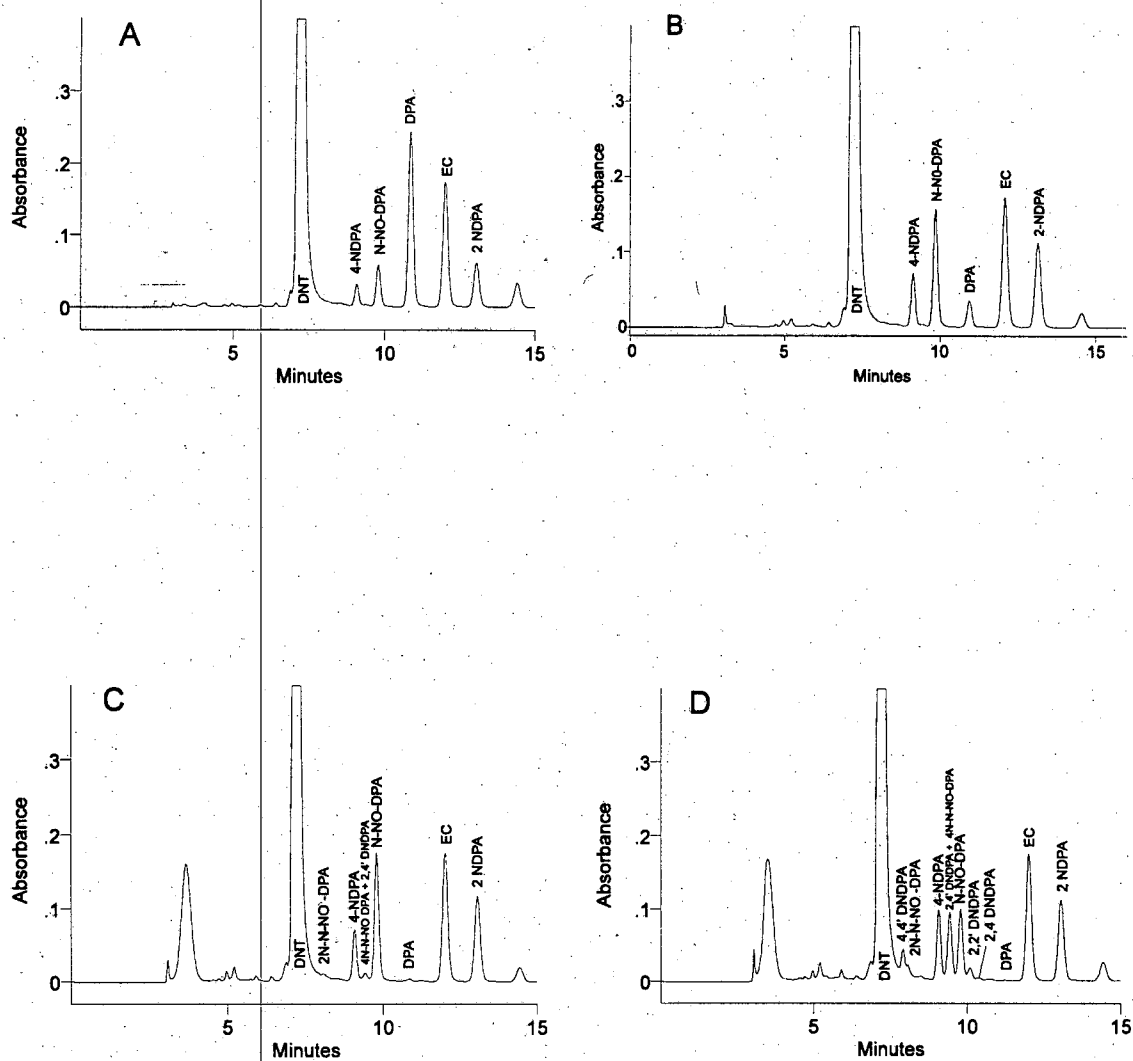


FIGURE 11-Chromatograms of a single base gun powder (FNH):

- A-) Original;
- B-) After 90 days of ageing at 65.5 °C;
- C-) After 120 days of ageing at 65.5 °C;
- D-) After 180 days of ageing at 65.5 °C.

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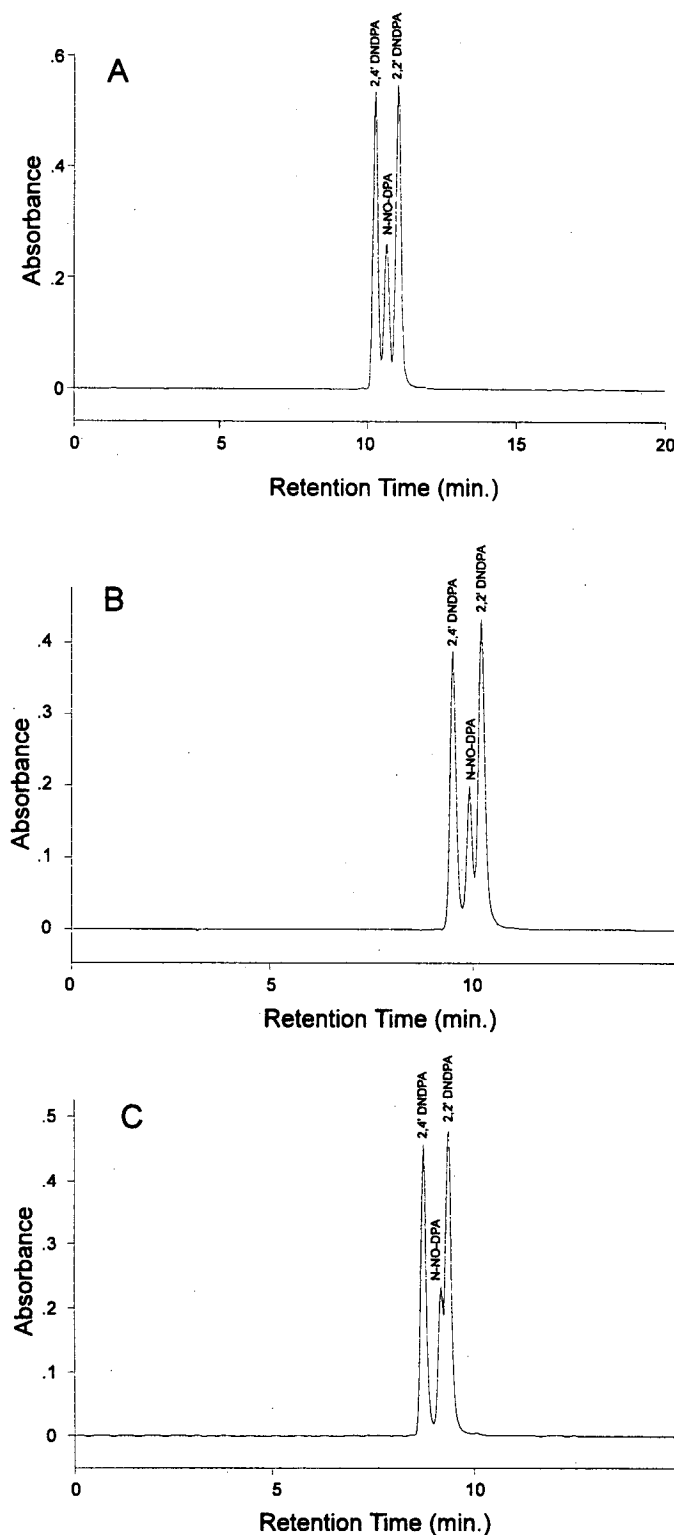


FIGURE 12 - Adjustements of the mobile phase:

A-) 69% ACN/31% water;

B-) 71% ACN/29% water;

C-) 73% ACN/27% water.

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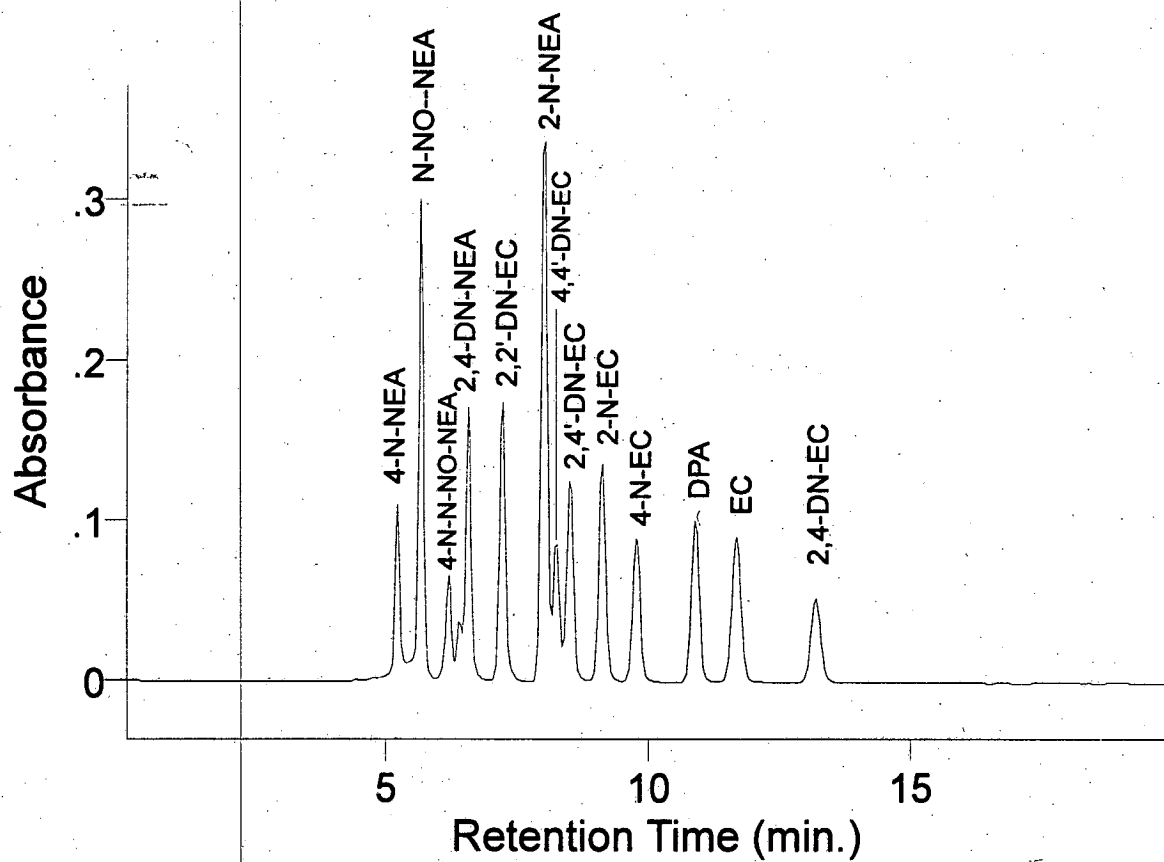


FIGURE 13 - Chromatogram of the major EC derivatives

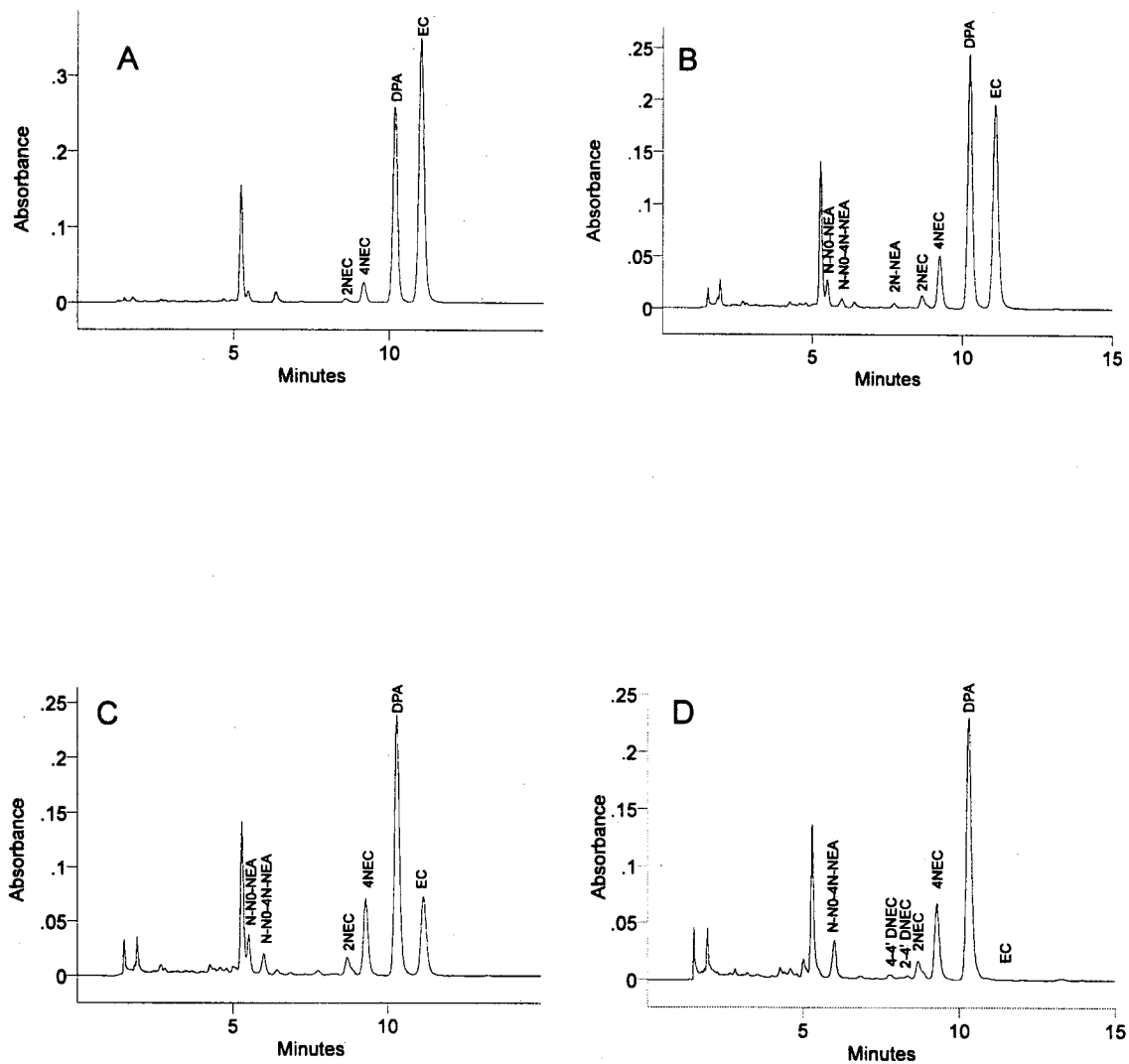


FIGURE 14 - Chromatograms of a double base gun powder (AKB 204):

- A-) Original;
- B-) After 90 days of ageing at 65.5 °C;
- C-) After 215 days of ageing at 65.5 °C;
- D-) After 360 days of ageing at 65.5 °C.

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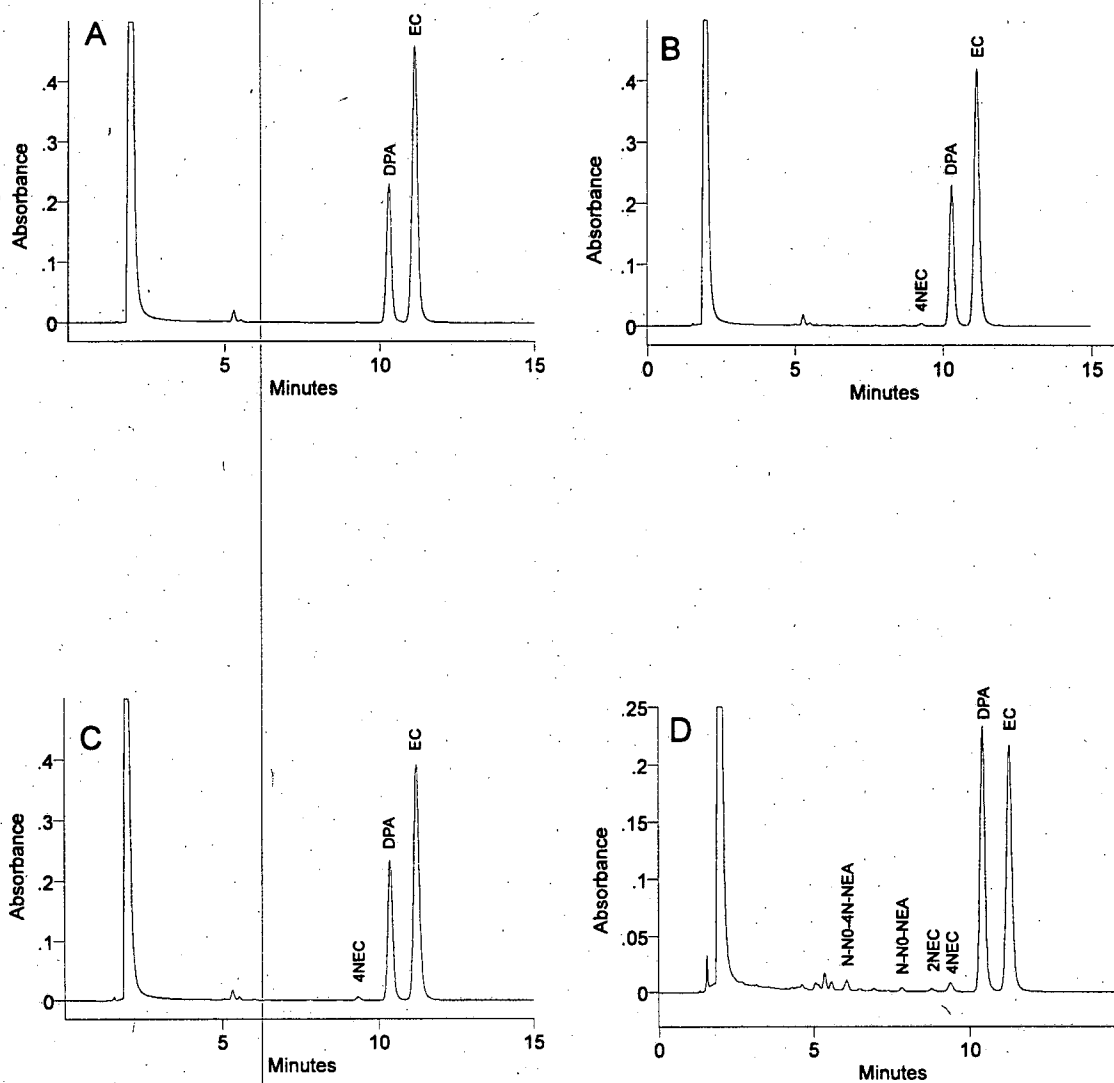


FIGURE 15 - Chromatograms of a triple base gun powder (SPCG):

A-) Original;

B-) After 90 days of ageing at 65.5 °C;

C-) After 120 days of ageing at 65.5 °C;

D-) After 623 days of ageing at 65.5 °C.

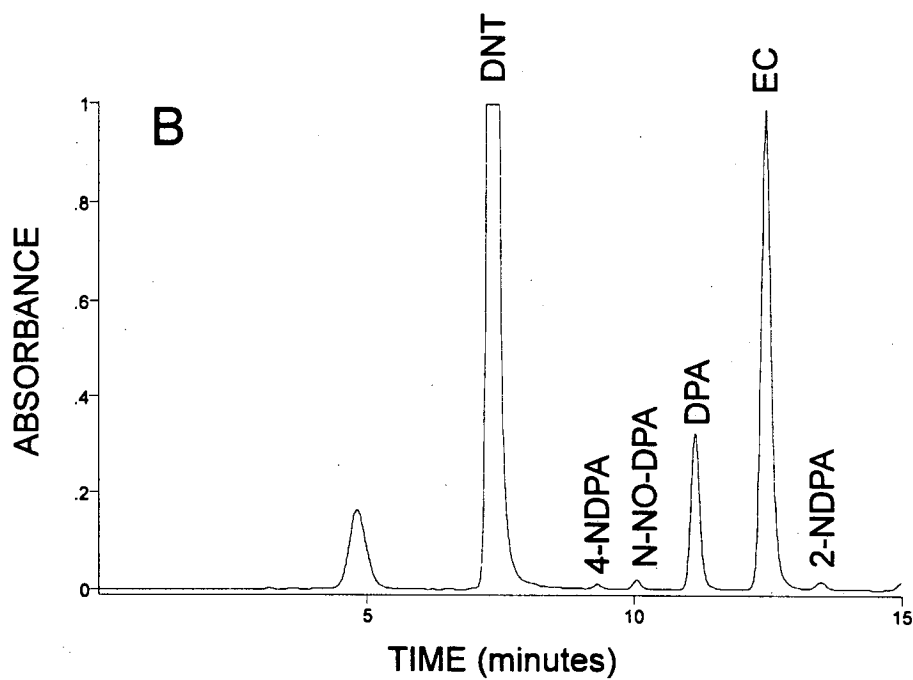
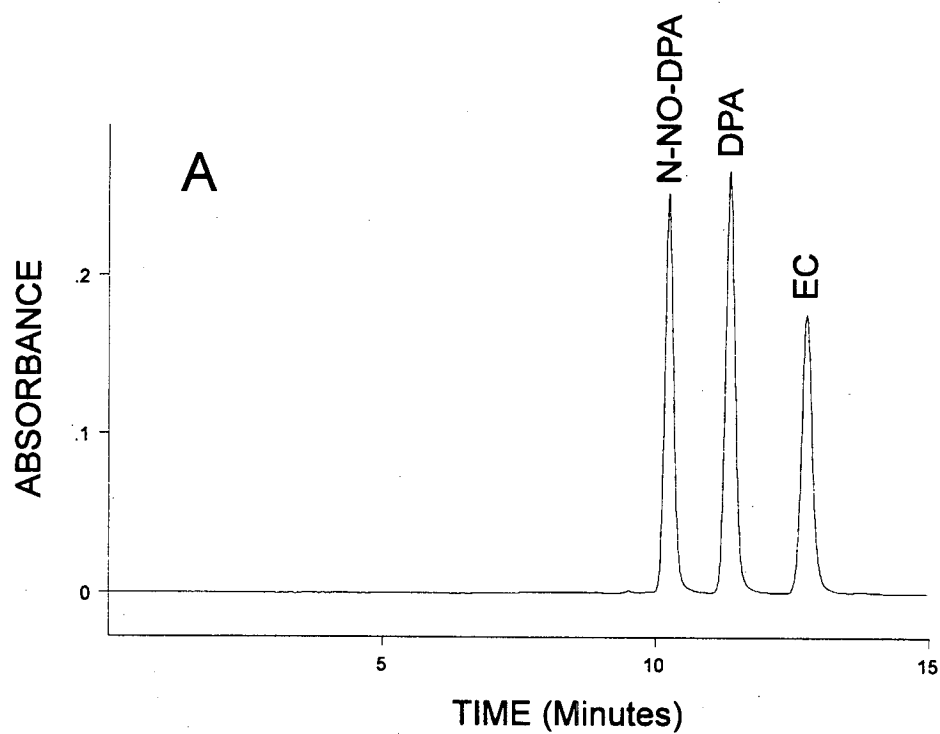


FIGURE 16- A-) Chromatogram of standard solution;
B-) Chromatogram of the M1 powder.

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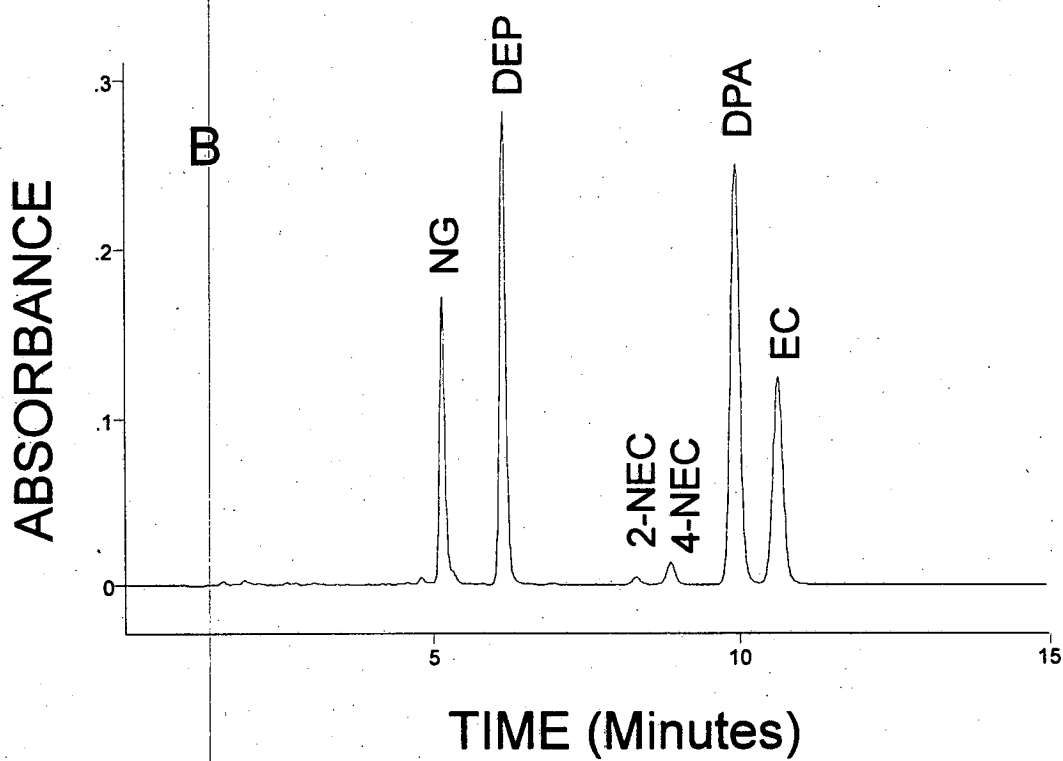
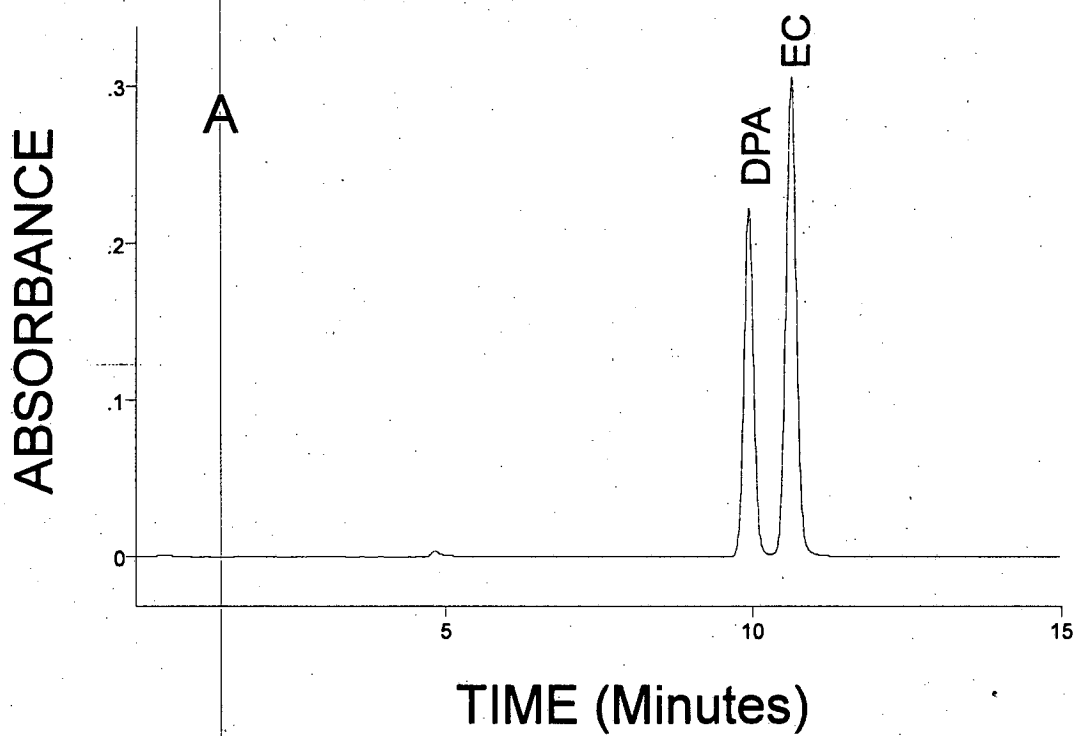


FIGURE 17- A-) Chromatogram of standard solution;
B-) Chromatogram of the M8 powder.

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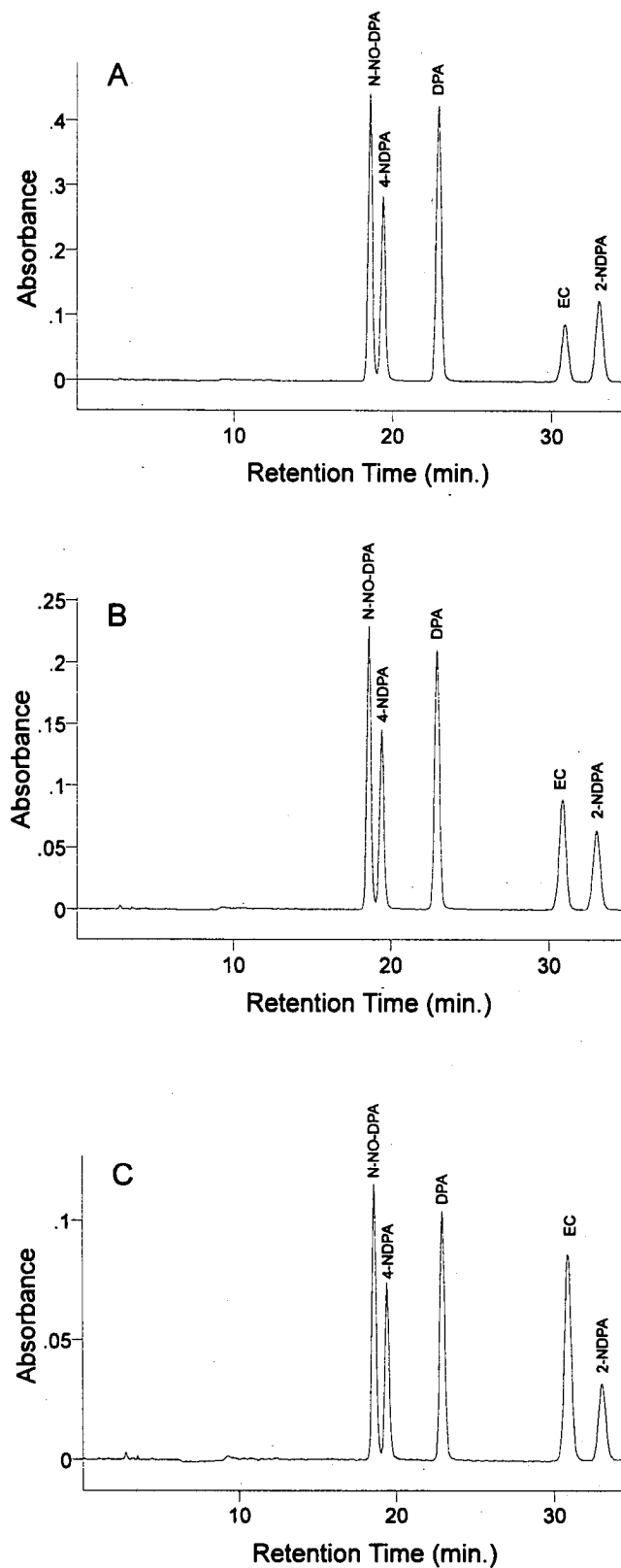


FIGURE 18 - Chromatograms for three standard solutions

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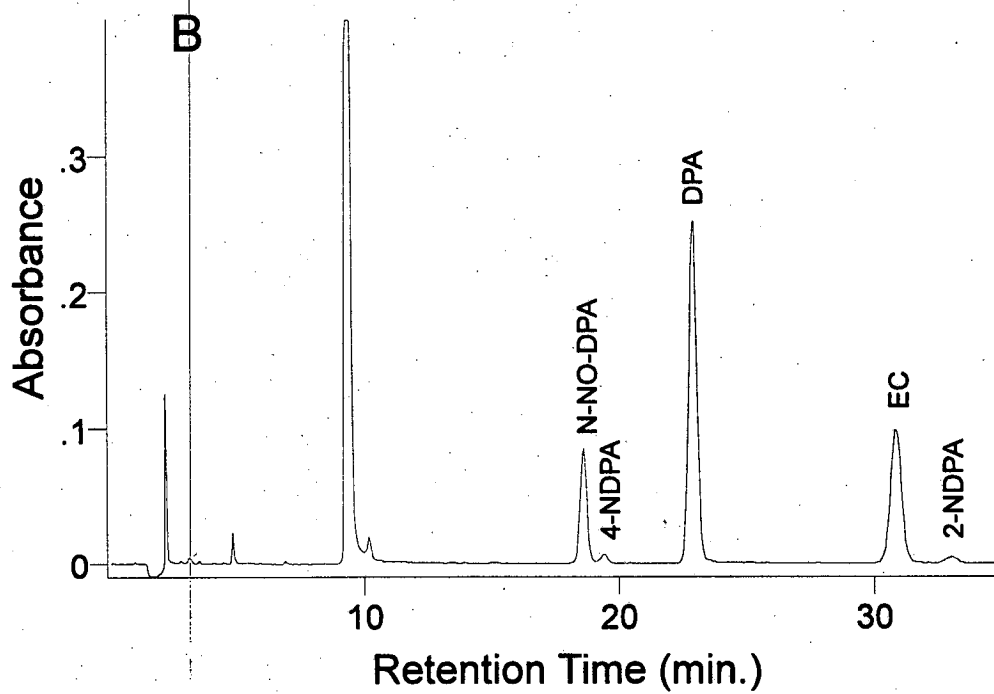
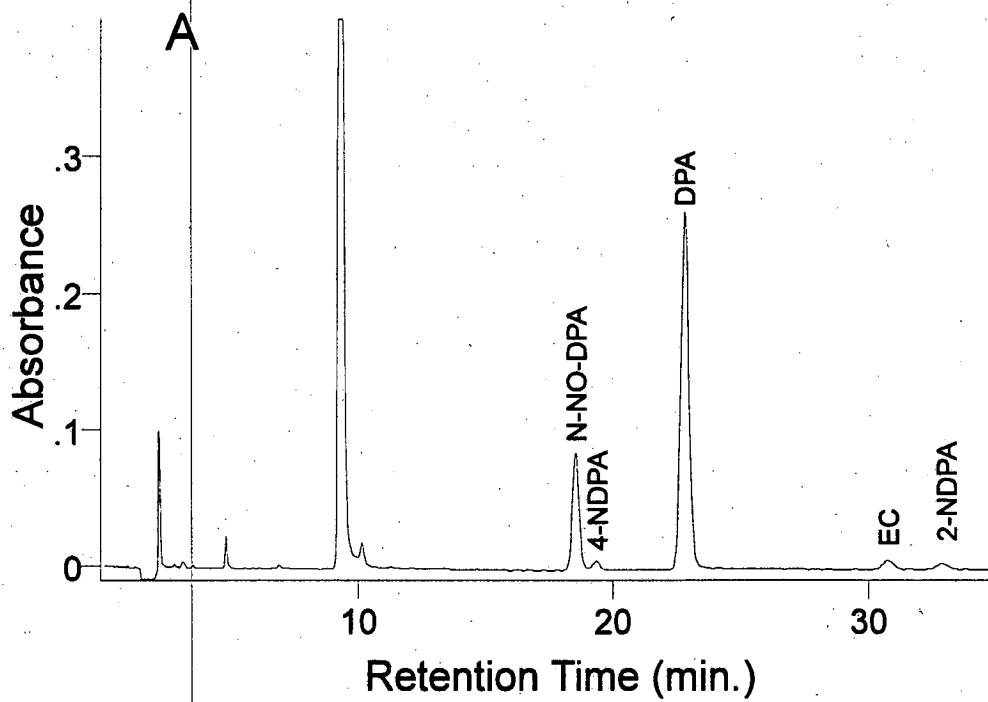


FIGURE 19 -Chromatograms of a ball powder:

- A-) Without the addition of the internal standard (EC);
- B-) With the addition of the internal standard (EC).

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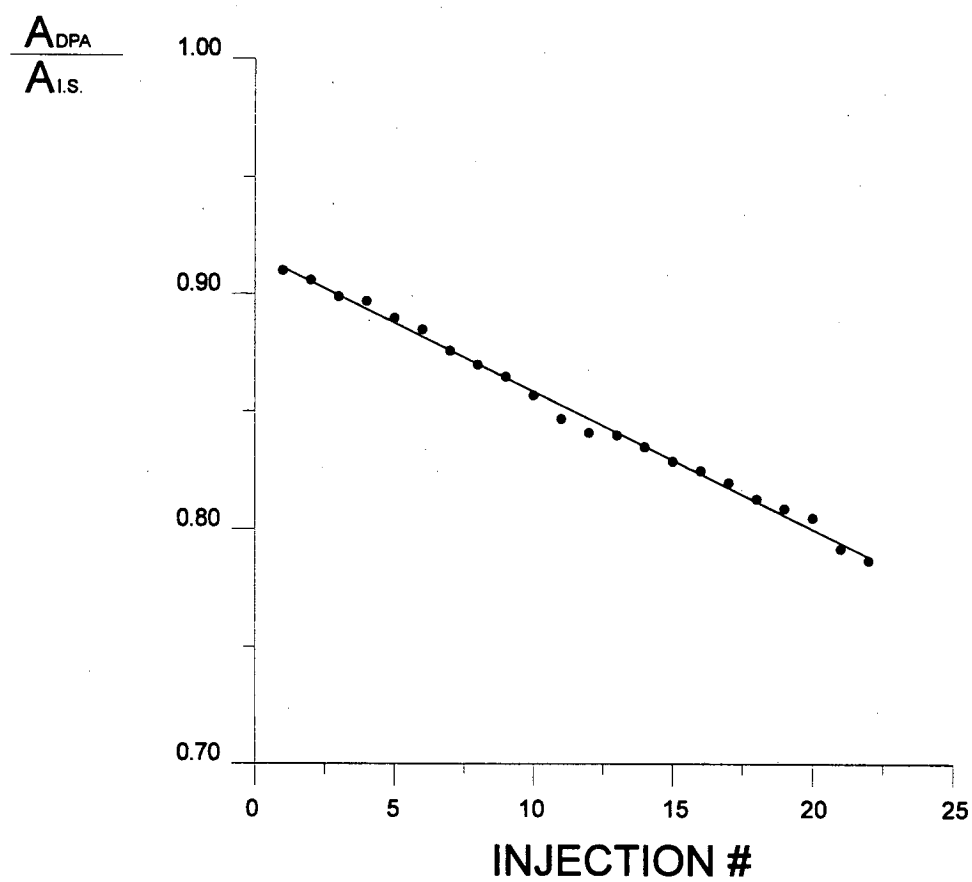


FIGURE 20 - Ratio of area of DPA peak and internal standard peak for a Hypersil column

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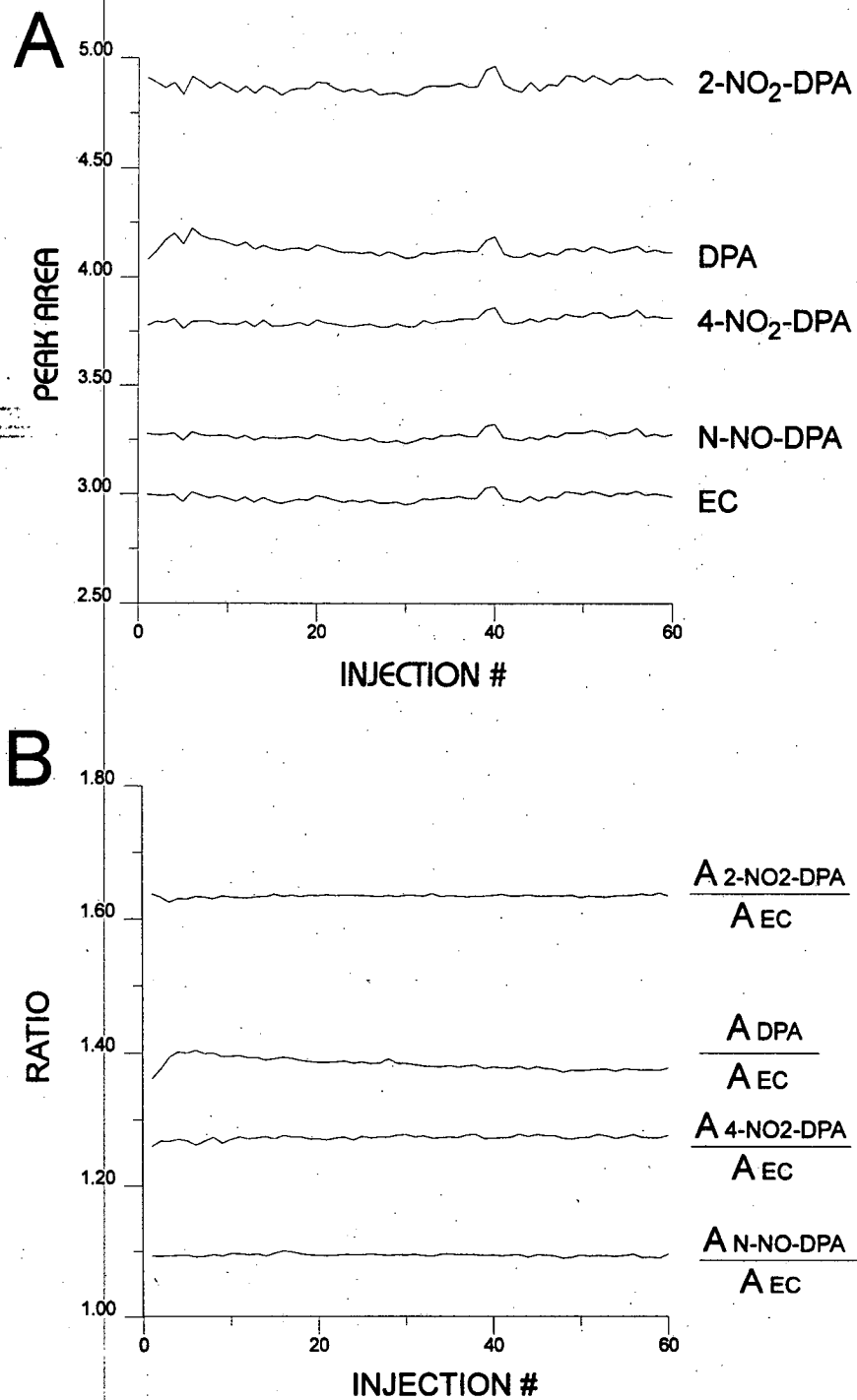


FIGURE 21- A-) Peak area of DPA and its first derivatives and the internal standard EC;
B-) Ratio of the peak area of DPA and its first derivatives to peak area of the
internal standard EC.

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TABLE I

Formulation of DPA-stabilized gunpowders used by the CF

POWDER	% NC	% DPA	% DNT	% OTHERS
C1 CMR (100)	91.0	>.5<1	7.0	
GBPA 122	82.5	1.1	--	DPP,1.13 NG,13.5
M1	85.0	1.0	10.0	DBP,5.0
FNH	84.0	1.0	10.0	DBP,5.0
NH	86.0	1.0	10.0	DBP,3.0
M10	98.0	1.0	--	
M6	87.0	1.0	10.0	
NC 1066	90.6	1.0	--	DAP,6.6
NC30	99.0	1.0	--	
PRB A6Y	DIFF.	.85 TO 1.5	--	
TD.NC.01.KDX	98.0	1.0	--	

Components such as inorganic compounds have been excluded.

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TABLE IIFormulation of EC-stabilized gunpowders used by the CF

POWDER	% NC	% NG	% NQ	% EC	% OTHERS
AKB 204	61	37.5	--	1.5	
BALLISTITE B	59.9	38.0	--	0.6	
BS NACO	93.6	--	--	1.2	NBS, 3.0
C 1011	90	--	--	>1.4	CAM, 6.0
M2	77.5	19.5	--	0.6	
M26	67.3	25.0	--	6.0	
M7	54.6	35.5	--	0.9	
M8	52.2	43.0	--	0.6	DEP, 3.0
M9	57.8	40.0	--	0.75	
N	19.0	18.7	55.0	7.3	
NQ	20.8	20.6	55.0	3.6	
SPCF	93.6	--	--	1.2	NBS, 3.0
SPCG (COOL)	20.0	8.8	60.0	2.0	DPP OR KS 9.2
SPCG	19.0	18.7	55.0	7.3	

Components such as inorganic compounds have been excluded.

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TABLE III

DPA daughter products and their abbreviations

NAME	ABBREVIATION
DIPHENYLAMINE	DPA
N-NITROSO DIPHENYLAMINE	N-NO-DPA
2-NITRO DIPHENYLAMINE	2 NDPA
4 -NITRO DIPHENYLAMINE	4 NDPA
4-NITRO-N-NITROSO DIPHENYLAMINE	4N-N-NO-DPA
2-NITRO-N-NITROSO DIPHENYLAMINE	2N-N-NO-DPA
4,4'-DINITRO DIPHENYLAMINE	4,4' DNDPA
2,4'-DINITRO DIPHENYLAMINE	2,4' DNDPA
2,2'-DINITRO DIPHENYLAMINE	2,2' DNDPA
2,4-DINITRODIPHENYLAMINE	2,4 DNDPA
2,6-DINITRO DIPHENYLAMINE	2,6 DNDPA
N-NITROSO-4,4'-DINITRO DIPHENYLAMINE	N-NO-4,4'-DNDPA
N-NITROSO-2,4'-DINITRO DIPHENYLAMINE	N-NO-2,4'-DNDPA
2,2',6-TRINITRO DIPHENYLAMINE	2,2',6 TNDPA
2,4,6-TRINITRO DIPHENYLAMINE	2,4,6 TNDPA
2,2',4-TRINITRO DIPHENYLAMINE	2,2',4 TNDPA
2,4',6-TRINITRO DIPHENYLAMINE	2,4',6 TNDPA
2,4,4'-TRINITRO DIPHENYLAMINE	2,4,4' TNDPA
2,2',4,4'-TETRANITRO DIPHENYLAMINE	2,2',4,4' TNDPA
2,2',4,6-TETRANITRO DIPHENYLAMINE	2,2',4,6 TNDPA
2,3',4,6-TETRANITRO DIPHENYLAMINE	2,3',4,6 TNDPA
2,2',6,6'-TETRANITRO DIPHENYLAMINE	2,2',6,6' TNDPA
2,4,4',6-TETRANITRO DIPHENYLAMINE	2,4,4',6 TNDPA
2,2',4',6-TETRANITRO DIPHENYLAMINE	2,2',4',6 TNDPA
2,2',4,4',6-PENTANITRO DIPHENYLAMINE	2,2',4,4',6 PNDPA
2,2',4,6,6'-PENTANITRO DIPHENYLAMINE	2,2',4,6,6' PNDPA
2,2',4,4',6,6'-HEXANITRO DIPHENYLAMINE	2,2',4,4',6,6' HNDPA

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TABLE IV

EC daughter products and their abbreviations

NAME	ABBREVIATION
ETHYLCENTRALITE	EC
4-NITRO ETHYLCENTRALITE	4-N-EC
2-NITRO ETHYLCENTRALITE	2-N-EC
2,4' DINITRO ETHYLCENTRALITE	2,4'-DN-EC
4,4' DINITRO ETHYLCENTRALITE	4,4'-DN-EC
2,2' DINITRO ETHYLCENTRALITE	2,2'-DN-EC
2,4 DI NITRO ETHYLCENTRALITE	2,4- DN-EC
2,2',4 TRI NITRO ETHYLCENTRALITE	2,2',4 -TN-EC
TETRANITRO ETHYLCENTRALITE	TETRANITROEC
N-NITROSO-N-ETHYLANILINE	N-NO-NEA
N-NITROSO-2-NITRO-N-ETHYLANILINE	N-NO-2N-NEA
N-NITROSO-4-NITRO-N-ETHYLANILINE	N-NO-4N-NEA
2-NITRO-N-ETHYLANILINE	2-N-NEA
4-NITRO N-ETYLANILINE	4-N-NEA
2,4-DI-NITRO-N-ETHYLANILINE	2,4-DN-NEA
2,4,6 TRI NITRO-N-ETHYLANILINE	2,4,6 TN-NEA
N,2,4,6, TETRANITRO-N-ETHYLANILINE	N,2,4,6,TN-NEA
2-NITRO ANILINE	2-N-A
4-NITRO ANILINE	4-N-A
2,4-DI NITRO ANILINE	2,4-DN-A
NITROBENZENE	NB
DINITROBENZENE	DNB
4-NITRO PHENOL	4-N-P

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TABLE V

Conditions for DPA-stabilized gunpowders

COLUMN	Lichrocart supersher, RP-18e, 3 μ m 25 cm X 4.6 mm E. Merck
SOLVANT	71 % ACN + 29 % Water
FLOW	0.5 ml/min.
COLUMN TEMPERATURE	28 °C
VOLUME INJECTED	5 μ L

TABLE VI

Retention times for various DPA daughter products

Product name	Retention time (min.)
2,2',4,4',6,6' HNDPA	2.82
2,4',6 TNDPA	5.31
2,2',4',6 TNDPA	5.86
NG	6.58 *
2,2',4,6,6' PNDPA	6.60
2,2',4,4',6 PNDPA	6.78
2,4,4',6 TNDPA	7.49
DNT Isomers	7.2 to 7.5
2,2',6,6' TNDPA	7.68
2,3',4,6 TNDPA	7.68
2,2',6 TNDPA	8.19
4,4' DNDPA	8.28
2,2',4,6 TNDPA	8.28
N-NO-2,4' DNDPA	8.28

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TABLE VI (cont)

2N-N-NO-DPA	8.49
2,4,6 TNDPA	8.49
2,6 DNDPA	8.67
2,2',4,4' TNDPA	8.77
2,4,4' TNDPA	8.90
N-NO-4,4' DNDPA	8.96
2,2',4 TNDPA	9.25
4 NDPA	9.59
4N-N-NO DPA	9.93
2,4' DNDPA	9.97
N-NO DPA	10.38
2,2' DNDPA	10.75
2,4 DNDPA	11.05
DPA	11.51
DAP	13.62
2 NDPA	13.92
DPP	16.25
DBP	22.62

* NG does not absorb at 254 nm this retention time was determined with the detector at 205 nm.

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TABLE VII

Change in retention times as the column ages

Derivative name	R.T. for new column	R.T. for aged column	Δ
2,4',6 TNDPA	5.31	5.15	1.03
2,2'4',6 TNDPA	5.86	5.68	1.03
2,2',4,6,6' PNDPA	6.6	6.37	1.04
2,4,4',6 TNDPA	7.49	7.24	1.04
2,2',6,6' TNDPA	7.68	7.38	1.04
2,2',6 TNDPA	8.19	7.87	1.04
4,4' DNDPA	8.28	7.93	1.04
2,2'4,6 TNDPA	8.28	7.94	1.04
N-NO-2,4' DNDPA	8.28	7.98	1.04
2N-N-NO-DPA	8.49	8.17	1.04
2,4,6 TNDPA	8.49	8.14	1.04
2,6 DNDPA	8.67	8.31	1.04
2,2',4,4' TNDPA	8.77	8.44	1.04
2,4,4' TNDPA	8.9	8.53	1.04
N-NO-4,4' DNDPA	8.96	8.57	1.04
2,2',4 TNDPA	9.25	8.88	1.04
4 NDPA	9.59	9.18	1.05
4N-N-NO DPA	9.93	9.5	1.05
2,4' DNDPA	9.97	9.54	1.05
N-NO DPA	10.38	9.88	1.05
2,2' DNDPA	10.75	10.24	1.05
2,4 DNDPA	11.05	10.48	1.05
DPA	11.51	10.94	1.05
2 NDPA	13.92	13.18	1.06

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TABLE VIIIConditions for EC-stabilized gunpowders

COLUMN	Lichrocart supersher, RP-18e, 3 μ m 25 cm X 4.6 mm E. Merck
SOLVANT	58 % ACN + 42 % Water
FLOW	1.0 ml/min.
COLUMN TEMPERATURE	28 °C
DETECTOR WAVELENGTH	254 nm
VOLUME INJECTED	5 μ L

TABLE IXRetention times for various EC daughter products

Product name	Retention Time
NQ	1.94
4-NITRO PHENOL	3.2
4-NITRO ANILINE	3.2
2,4-DI NITRO ANILINE	3.84
2-NITRO ANILINE	3.93
DINITROBENZENE	4.68
N-NITROSO 2-NITRO N-ETHYLANILINE	4.95
NITROBENZENE	5.13
4-NITRO N-ETYL ANILINE	5.29
NG	5.59 *
N-NITROSO-N-ETHYLANILINE	5.69
4-NITRO-N-NITROSO -N-ETHYLANILINE	6.22
METHYL CENTRALITE	6.22

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TABLE IX (con't)

N,2,4,6, TETRANITRO -N-ETHYLANILINE	6.49
2,4 DI NITRO -N-ETHYL ANILINE	6.59
DEP	6.64
2,4,6 TRI NITRO- N-ETHYLANILINE	7.12
2,2' DINITRO ETHYLCENTRALITE	7.12
CAMPHOR	7.5
2-NITRO-N-ETHYLANILINE	8.02
4,4' DINITRO ETHYLCENTRALITE	8.25
2,4' DINITRO ETHYLCENTRALITE	8.52
TETRANITRO ETHYLCENTRALITE	9.08
2-NITRO ETHYLCENTRALITE	9.12
2,2',4 TRI NITRO ETHYLCENTRALITE	9.72
4-NITRO ETHYLCENTRALITE	9.79
DIPHENYLAMINE	10.87
ETHYLCENTRALITE	11.72
2,4 DI NITRO ETHYLCENTRALITE	13.12
DPP	13.09
DAP	13.89
DBP	28.2

* NG does not absorb at 254 nm this retention time was determined with the detector at 205 nm.

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TABLE X

Data and linear regression results for the external standard calibration

DPA		N-NO-DPA	
Conc. (mg/ml)	Area ($\mu\text{V}\cdot\text{s}$)	Conc. (mg/ml)	Area ($\mu\text{V}\cdot\text{s}$)
0.2420	9494760	0.2521	8199050
0.1210	4667265	0.1261	4199460
0.0605	2289440	0.0631	2138115
Slope	39727007	Slope	32022381
Y-intercept	-124308	Y-intercept	134913
Corr. coeff	0.9999	Corr. coeff	0.9999

TABLE XI

Results of concentration of various DPA derivatives with and without NC precipitation (mean of three analysis)

Derivative	% without NC precipitation	σ	% with NC Precipitation	σ
N-NODPA	0.116	0.001	0.118	0.004
2-NO ₂ -DPA	0.296	0.001	0.299	0.012
4-NO ₂ -DPA	0.117	0.001	0.118	0.005
2-NO ₂ -N-NO-DPA	0.054	0.002	0.055	0.003
4-NO ₂ -N-NO-DPA	0.499	0.001	0.509	0.018
2,4-di-NO ₂ -DPA	0.016	0.001	0.018	0.001
2,2'-di-NO ₂ -DPA	0.099	0.001	0.101	0.004
4,4'-di-NO ₂ -DPA	0.244	0.001	0.242	0.010

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TABLE XII

Results of % of EC with and without NC precipitation. (mean of three analysis)

POWDER	% of EC without NC precipitation	σ	% of EC with NC precipitation	σ
M8	0.49	0.02	0.47	0.01
AKB 204	0.19	0.01	0.19	0.01
SPCG	6.99	0.05	7.05	0.02
SPCG aged	3.65	0.01	3.63	0.02

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TABLE XIII

Multiinjections results for DPA method

CALIBRATION # 1	DPA KF _i	N-NO-DPA KF _i	CALIBRATION # 2	DPA KF _i	N-NO-DPA KF _i
	1.4007	1.5999		1.3827	1.5938
	1.3782	1.5963		1.3655	1.5991
	1.3713	1.6064		1.3610	1.6103
INJECTION #	% DPA	% N-NO-DPA	INJECTION #	% DPA	% N-NO-DPA
1	0.13	0.57	13	0.13	0.56
2	0.13	0.57	14	0.13	0.56
3	0.12	0.57	15	0.13	0.56
4	0.13	0.57	16	0.13	0.56
5	0.13	0.56	17	0.13	0.56
6	0.12	0.56	18	0.13	0.56
7	0.13	0.56	19	0.13	0.56
8	0.13	0.56	20	0.13	0.56
9	0.13	0.56	21	0.13	0.57
10	0.13	0.56	22	0.12	0.56
11	0.12	0.56	23	0.12	0.56
12	0.13	0.56	24	0.12	0.56

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TABLE XIII (cont'd)

CALIBRATION #3	DPA KF _i	N-NO-DPA KF _i	CALIBRATION #4	DPA KF _i	N-NO-DPA KF _i
	1.3766	1.6044		1.3650	1.6025
	1.3554	1.5967		1.3500	1.5968
	1.3515	1.6073		1.3464	1.6075
INJECTION #	% DPA	% N-NO-DPA	INJECTION #	% DPA	% N-NO-DPA
25	0.13	0.57	37	0.13	0.57
26	0.13	0.57	38	0.13	0.57
27	0.13	0.57	39	0.13	0.57
28	0.13	0.56	40	0.13	0.57
29	0.13	0.56	41	0.13	0.56
30	0.13	0.56	42	0.13	0.56
31	0.13	0.56	43	0.13	0.56
32	0.13	0.56	44	0.13	0.56
33	0.13	0.56	45	0.13	0.56
34	0.13	0.56	46	0.13	0.56
35	0.13	0.56	47	0.13	0.56
36	0.13	0.56	48	0.13	0.56

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TABLE XIII (cont'd)

CALIBRATION # 5	DPA KF _i	N-NO-DPA KF _i	CALIBRATION # 6	DPA KF _i	N-NO-DPA KF _i
	1.3512	1.5967		1.3528	1.5982
	1.3460	1.5973		1.3482	1.5978
	1.3449	1.6048		1.3505	1.6098
INJECTION #	% DPA	% N-NO-DPA	INJECTION #	% DPA	% N-NO-DPA
49	0.13	0.57	61	0.12	0.57
50	0.12	0.57	62	0.12	0.57
51	0.12	0.57	63	0.13	0.57
52	0.12	0.57	64	0.13	0.57
53	0.13	0.56	65	0.13	0.57
54	0.13	0.56	66	0.14	0.56
55	0.12	0.56	67	0.13	0.56
56	0.13	0.56	68	0.13	0.57
57	0.12	0.56	69	0.13	0.56
58	0.12	0.56	70	0.13	0.56
59	0.12	0.56	71	0.13	0.56
60	0.12	0.56	72	0.13	0.56

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TABLE XIV

Multiinjections results for EC method

CALIBRATION #1	EC KF ₁	CALIBRATION #2	EC KF ₁
	0.7140		0.6957
	0.6735		0.6592
	0.7143		0.701
INJECTION #	% EC	INJECTION #	% EC
1	0.42	13	0.43
2	0.43	14	0.43
3	0.43	15	0.43
4	0.43	16	0.43
5	0.44	17	0.43
6	0.44	18	0.43
7	0.44	19	0.43
8	0.44	20	0.43
9	0.44	21	0.42
10	0.44	22	0.42
11	0.44	23	0.42
12	0.44	24	0.42

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TABLE XIV (con't)

CALIBRATION # 3	EC KF ₁	CALIBRATION # 4	EC KF ₁
	0.6963	0.6966	
	0.6618	0.6628	
	0.7030	0.7040	
INJECTION #	% EC	INJECTION #	% EC
25	0.42	37	0.42
26	0.42	38	0.43
27	0.42	39	0.43
28	0.42	40	0.43
29	0.42	41	0.43
30	0.43	42	0.43
31	0.43	43	0.42
32	0.43	44	0.42
33	0.42	45	0.42
34	0.42	46	0.42
35	0.42	47	0.42
36	0.42	48	0.42

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TABLE XIV (con't)

CALIBRATION # 5	EC KF _i	CALIBRATION # 6	EC KF _i
	0.6972		0.7033
	0.6633		0.6701
	0.6951		0.7120
INJECTION #	% EC	INJECTION #	% EC
49	0.43	61	0.43
50	0.42	62	0.43
51	0.42	63	0.42
52	0.42	64	0.42
53	0.42	65	0.42
54	0.43	66	0.42
55	0.43	67	0.42
56	0.43	68	0.42
57	0.43	69	0.42
58	0.42	70	0.42
59	0.42	71	0.42
60	0.42	72	0.42

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TABLE XVConsistency of the results over a period of time

PROPELLANT	DATE	% DPA	% N-NO-DPA	% EC
FNH Not aged	OCTOBER 93	0.78	0.17	N/A
	SEPTEMBER 94	0.79	0.17	N/A
FNH aged	JANUARY 93	0.13	0.59	N/A
	JUNE 93	0.13	0.59	N/A
AKB Not aged	JUNE 93	N/A	N/A	1.27
	OCTOBER 94	N/A	N/A	1.21
AKB aged	JUNE 93	N/A	N/A	0.19
	OCTOBER 94	N/A	N/A	0.18

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TABLE XVI

Comparison between Canada and France

POWDER 1				
	FRANCE		CANADA	
	% DPA	% N-NO-DPA	% DPA	% N-NO-DPA
1	0.95	0.18	0.95	0.19
2	0.97	0.18	0.94	0.19
3	--	--	0.94	0.19

POWDER 2				
	FRANCE		CANADA	
	% DPA	% N-NO-DPA	% DPA	% N-NO-DPA
1	0.48	0.15	0.40	0.18
2	0.48	0.16	0.39	0.18
3	--	--	0.39	0.17

POWDER 3				
	FRANCE		CANADA	
	% DPA	% N-NO-DPA	% DPA	% N-NO-DPA
1	0.04	0.25	0.02	0.25
2	0.04	0.25	0.02	0.25
3	--	--	0.02	0.27

TABLE XVII

Results of analysis of three grains of powder 2

	FRANCE		CANADA	
	% DPA	% N-NO-DPA	% DPA	% N-NO-DPA
GRAIN # 1	0.25	0.08	0.63	0.15
GRAIN # 2	0.48	0.08	0.20	0.13
GRAIN # 3	0.81	0.19	0.54	0.10

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TABLE XVIIISentencing criteria

% of original stabilizer remaining ¹	years until next analysis
80-100	5
60-80	3
40-60	2
20-40	1 ²
< 20	Retest + immediate disposal

Note 1 : defined as the ratio of residual effective stabilizer and the amount of original stabilizer in the gun powder formulation. The residual effective stabilizer is defined as the concentration of DPA + 85 % of the concentration of N-NO-DPA for DPA-stabilized gun powder and as the concentration of EC for EC-stabilized gun powders.

Note 2: These gun powders should be used in priority and should not be send outside Canada.

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13. **ABSTRACT** (a brief and factual summary of the document. It may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall begin with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (S), (C), (R), or (U). It is not necessary to include here abstracts in both official languages unless the text is bilingual).

This document is the final report required by the task from the Directorate of Ammunition Engineering Service aimed to develop modern methods to monitor the chemical stability and remaining safelife of the gun powders stocked by the Canadian Forces. Initially, there is a review of the chemistry of propellant ageing and the various techniques available to monitor the chemical stability. This is followed by the description of the development of two fast, reliable and efficient high performance liquid chromatography methods. Finally, the application of these two methods for the surveillance programme of diphenylamine or ethycentralite-stabilized gun propellants are discussed.

14. **KEYWORDS, DESCRIPTORS or IDENTIFIERS** (technically meaningful terms or short phrases that characterize a document and could be helpful in cataloguing the document. They should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location may also be included. If possible keywords should be selected from a published thesaurus. e.g. Thesaurus of Engineering and Scientific Terms (TEST) and that thesaurus-identified. If it is not possible to select indexing terms which are Unclassified, the classification of each could be indicated as with the title.)

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